

AD-A129 031

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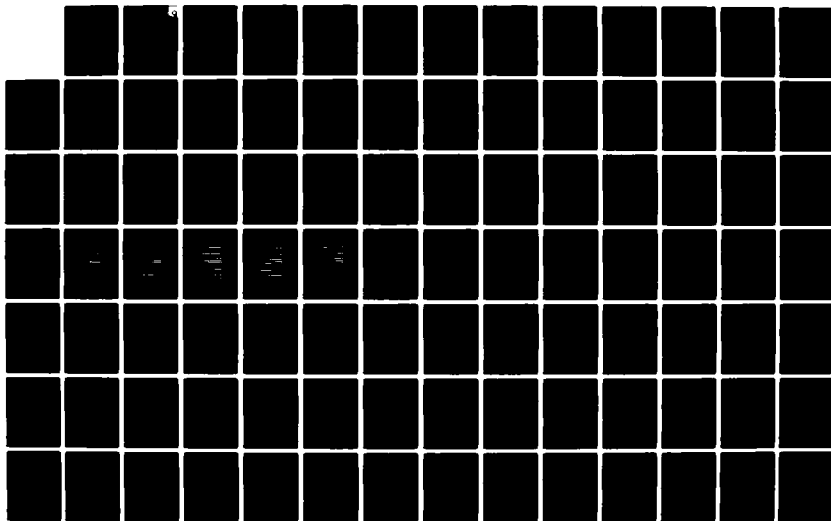
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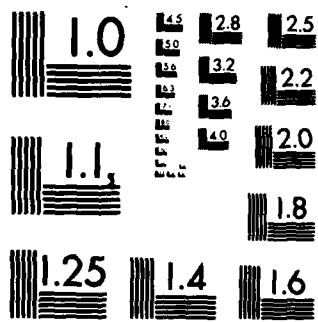
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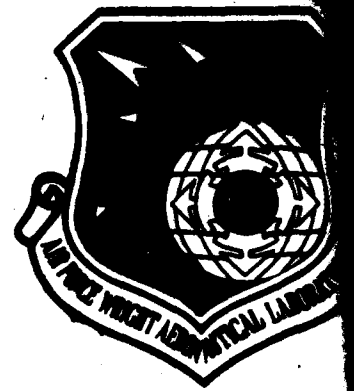
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AFWAL-TR-81-2056
Part II, Vol II



REFINING OF MILITARY JET FUELS FROM SHALE OIL

Part II, Vol II
In Situ Shale Oil Process Data

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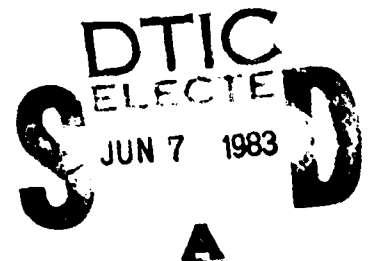
ASHLAND PETROLEUM COMPANY
ASHLAND RESEARCH AND DEVELOPMENT
ASHLAND, KENTUCKY 41101

MARCH 1982

INTERIM TECHNICAL REPORT FOR PERIOD
June 1979 - October 1980

Approved for Public Release; Distribution Unlimited

AERO PROPULSION LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
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|---|-----------------------|--|
| 1. REPORT NUMBER | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
| AFWAL-TR-81-2056, Part II, Vol II | AD-A129031 | |
| 4. TITLE (and Subtitle) | | 5. TYPE OF REPORT & PERIOD COVERED |
| REFINING OF MILITARY JET FUELS FROM SHALE OIL PART II, VOL II (In Situ Shale Oil Process Data) | | Interim Report for Period June 1979 - October 1980 |
| | | 6. PERFORMING ORG. REPORT NUMBER |
| | | |
| 7. AUTHOR(s) | | 8. CONTRACT OR GRANT NUMBER(s) |
| H. R. Moore D. A. Fabry L. M. Henton C. A. Johnson | | F33615-78-C-2080 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS | | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS |
| Ashland Petroleum Company Ashland Research and Development P.O. Box 391, Ashland KY 41101 | | PE 63215F WU 24800004 |
| 11. CONTROLLING OFFICE NAME AND ADDRESS | | 12. REPORT DATE |
| Aero Propulsion Laboratory (AFWAL/POSF) Air Force Wright Aeronautical Labs AFSC Wright-Patterson AFB, Ohio 45433 | | March 1982 |
| | | 13. NUMBER OF PAGES |
| | | 287 |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) | | 15. SECURITY CLASS. (of this report) |
| | | Unclassified |
| | | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |
| | | |
| 16. DISTRIBUTION STATEMENT (of this Report) | | |
| Approved for public release; distribution unlimited. | | |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) | | |
| | | |
| 18. SUPPLEMENTARY NOTES | | |
| | | |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) | | |
| Shale Oil Refining Basic Nitrogen Extraction JP-4 Jet Fuel Total Nitrogen Reforming JP-8 Jet Fuel Fluid Catalytic Cracking Hydrotreating Guardcase Hydrotreater Denitrogenation Automatic Saturation | | |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) | | |
| Phase II work performed was directed toward the completion of two primary tasks. Task I under this phase was directed at evaluating the effect of operating conditions on material quality, energy balances, product composition and economics. Task II was directed at obtaining scale-up data for those unit operations of the Phase I process requiring laboratory data to confirm preliminary estimates. This volume presents the data generated on the Occidental in situ crude shale oil. | | |

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FOREWORD

This project was sponsored by the U. S. Air Force Wright Aeronautical Laboratories (AFWAL), Air Force Systems Command, under Contract No. F33615-78-C-2080. The work herein was performed during the period June 15, 1979 to October 30, 1980 under Program Elements 62203F and 63215F, Work Units 30480504 and 24800004, respectively. A discussion of the entire Ashland effort under this contract can be found in a series of six reports (AFWAL-TR-81-2056) entitled "Refining of Military Jet Fuels from Shale Oil", Parts I, II, III, and IV (Part II consists of three volumes). This report is Volume II of Part II which describes the evaluation via the EXTRACTACRACKING Process of the in situ Occidental shale oil. The cognizant Air Force Project Scientist was Dr. Ronald D. Butler. We must give recognition to Carolyn Honaker for her assistance in preparing this report.

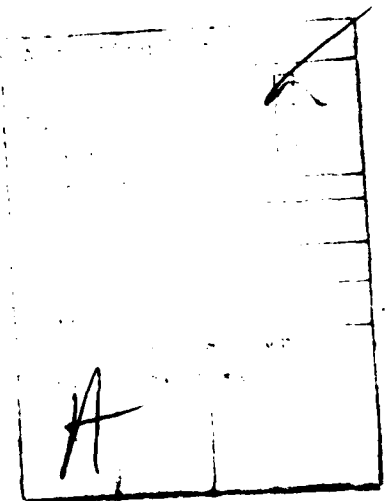


TABLE OF CONTENTS

VOLUME II

| | | <u>PAGE</u> |
|----------------|-------------------------------------|-------------|
| <u>SECTION</u> | | |
| I | INTRODUCTION..... | 1 |
| II | CRUDE SHALE ANALYSIS..... | 4 |
| | SUMMARY..... | 4 |
| | OBJECTIVE | 4 |
| | MECHANICAL DESCRIPTION..... | 4 |
| | EXPERIMENTAL..... | 5 |
| | EXPERIMENTAL RESULTS..... | 6 |
| | DISCUSSION..... | 15 |
| | CONCLUSIONS..... | 15 |
| III | CRUDE SHALE OIL HYDROTREATER..... | 16 |
| | 1. PARAMETER VARIATION STUDIES..... | 17 |
| | SUMMARY..... | 17 |
| | OBJECTIVE..... | 19 |
| | MECHANICAL DESCRIPTION..... | 19 |
| | CHEMICAL/CATALYST DESCRIPTION.... | 21 |
| | FEEDSTOCK..... | 21 |
| | EXPERIMENTAL..... | 22 |
| | EXPERIMENTAL RUN PREFIX 111..... | 23 |
| | EXPERIMENTAL RUN PREFIX 112..... | 26 |

TABLE OF CONTENTS (CONT'D)

| <u>SECTION</u> | <u>PAGE</u> |
|---|-------------|
| EXPERIMENTAL RUN PREFIX 113..... | 26 |
| EXPERIMENTAL RUN PREFIX 121..... | 29 |
| EXPERIMENTAL RUN PREFIX 122..... | 32 |
| EXPERIMENTAL RUN PREFIX 123..... | 37 |
| EXPERIMENTAL RESULTS..... | 37 |
| DISCUSSION..... | 58 |
| 2. M-SERIES STUDIES..... | 59 |
| SUMMARY..... | 59 |
| OBJECTIVES..... | 68 |
| UNIT DESCRIPTION..... | 68 |
| EXPERIMENTAL..... | 68 |
| FEEDSTOCK..... | 70 |
| RESULTS..... | 70 |
| DISCUSSION..... | 70 |
| 3. CRUDE SHALE OIL HYDROTREATER AGING.... | 80 |
| SUMMARY..... | 80 |
| OBJECTIVES..... | 80 |
| UNIT DESCRIPTION..... | 80 |
| FEEDSTOCK..... | 82 |
| EXPERIMENTAL..... | 82 |
| RESULTS..... | 85 |
| DISCUSSION..... | 99 |

TABLE OF CONTENTS (CONT'D)

| <u>SECTION</u> | | <u>PAGE</u> |
|----------------|---|-------------|
| IV | FLUID CATALYTIC CRACKING OF IN SITU SHALE OIL..... | 100 |
| 1. | MAT TESTS - FRESH FEED..... | 101 |
| | SUMMARY..... | 101 |
| | OBJECTIVES..... | 102 |
| | UNIT DESCRIPTION..... | 102 |
| | EXPERIMENTAL..... | 103 |
| | FEEDSTOCK..... | 104 |
| | RESULTS..... | 105 |
| | DISCUSSION..... | 105 |
| | RECOMMENDATIONS AND CONCLUSIONS.. | 125 |
| 2. | FCR PROCESSING - M-SERIES (FRESH FEED)..... | 126 |
| | SUMMARY..... | 126 |
| | OBJECTIVES..... | 126 |
| | UNIT DESCRIPTION..... | 126 |
| | FEEDSTOCK..... | 127 |
| | EXPERIMENTAL..... | 128 |
| | RESULTS..... | 128 |
| | DISCUSSION..... | 131 |
| | RECOMMENDATIONS AND CONCLUSIONS.. | 131 |
| 3. | FCR PROCESSING - OXY SAMPLE (FRESH FEED)..... | 132 |
| | SUMMARY..... | 132 |
| | OBJECTIVES..... | 132 |

TABLE OF CONTENTS (CONT'D)

| <u>SECTION</u> | <u>PAGE</u> |
|--|-------------|
| EXPERIMENTAL..... | 133 |
| UNIT DESCRIPTION..... | 133 |
| FEEDSTOCK..... | 133 |
| DISCUSSION..... | 138 |
| RECOMMENDATIONS AND CONCLUSIONS.. | 139 |
| 3. MAT TESTS - RECYCLE..... | 139 |
| SUMMARY..... | 139 |
| OBJECTIVES..... | 140 |
| UNIT DESCRIPTION..... | 140 |
| EXPERIMENTAL..... | 140 |
| FEEDSTOCK..... | 140 |
| RESULTS..... | 140 |
| DISCUSSION..... | 140 |
| RECOMMENDATIONS AND CONCLUSIONS.. | 144 |
| V EXTRACTION..... | 145 |
| SUMMARY..... | 145 |
| OBJECTIVE | 146 |
| MECHANICAL DESCRIPTION..... | 146 |
| CHEMICAL DESCRIPTION..... | 147 |
| EXPERIMENTAL PROCEDURE..... | 147 |
| 1. SCREENING STUDY..... | 147 |
| 2. CONTINUOUS EXTRACTION OF M-SERIES SAMPLES..... | 148 |

TABLE OF CONTENTS (CONT'D)

| <u>SECTION</u> | <u>PAGE</u> |
|--|-------------|
| 3. CONTINUOUS EXTRACTION OF IN SITU RETORTED SHALE OIL..... | 149 |
| EXPERIMENTAL RESULTS..... | 150 |
| 1. SCREENING STUDY..... | 150 |
| 2. M-SERIES..... | 153 |
| 3. IN SITU RETORTED SHALE OIL..... | 156 |
| DISCUSSION OF RESULTS..... | 156 |
| 1. PRELIMINARY SCREENING STUDY..... | 156 |
| 2. M-SERIES..... | 164 |
| 3. IN SITU RETORTED SHALE OIL..... | 164 |
| CONCLUSIONS..... | 166 |
| VI RECYCLE OIL HYDROTREATING..... | 169 |
| SUMMARY..... | 169 |
| OBJECTIVES..... | 169 |
| FEEDSTOCKS..... | 169 |
| EQUIPMENT..... | 170 |
| EXPERIMENTAL PROCEDURE..... | 174 |
| RESULTS..... | 176 |
| DISCUSSION OF RESULTS..... | 178 |
| CONCLUSIONS/RECOMMENDATIONS..... | 182 |
| VII GUARDCASE HYDROTREATING..... | 183 |
| 1. M-SERIES GUARDCASE HYDROTREATING..... | 183 |
| SUMMARY..... | 183 |

TABLE OF CONTENTS (CONT'D)

| <u>SECTION</u> | <u>PAGE</u> |
|---|-------------|
| OBJECTIVES..... | 184 |
| MECHANICAL DESCRIPTION..... | 184 |
| CHEMICAL AND CATALYST DESCRIPTIONS..... | 186 |
| EXPERIMENTAL PROCEDURE..... | 187 |
| EXPERIMENTAL RESULTS..... | 189 |
| INITIAL HYDROTREATING..... | 189 |
| REHYDROTREATING..... | 193 |
| DISCUSSION OF RESULTS..... | 193 |
| INITIAL HYDROTREATING..... | 193 |
| REHYDROTREATING..... | 195 |
| CONCLUSIONS..... | 195 |
| 2. GUARDCASE HYDROTREATING..... | 196 |
| SUMMARY..... | 196 |
| OBJECTIVES..... | 197 |
| MECHANICAL DESCRIPTION..... | 197 |
| CHEMICAL AND CATALYST DESCRIPTION..... | 197 |
| DESCRIPTION OF EXPERIMENTAL PROCEDURE..... | 198 |
| EXPERIMENTAL RESULTS..... | 200 |
| DISCUSSION OF RESULTS..... | 206 |
| CONCLUSIONS..... | 206 |
| VIII FREEZE POINT MODIFICATION..... | 207 |

TABLE OF CONTENTS (CONT'D)

| <u>SECTION</u> | <u>PAGE</u> |
|--|-------------|
| 1. SIMULATION OF FREEZE POINT MODIFICATION BY BLENDS OF JET FUEL AND NORMAL PARAFFINS..... | 207 |
| SUMMARY..... | 207 |
| OBJECTIVES..... | 208 |
| EQUIPMENT AND EXPERIMENTAL..... | 208 |
| FEEDSTOCKS..... | 210 |
| RESULTS..... | 210 |
| DISCUSSION..... | 233 |
| 2. M-SERIES..... | 236 |
| SUMMARY..... | 236 |
| OBJECTIVES..... | 236 |
| EQUIPMENT AND EXPERIMENTAL..... | 237 |
| FEEDSTOCK..... | 237 |
| RESULTS..... | 237 |
| DISCUSSION..... | 237 |
| RECOMMENDATIONS AND CONCLUSIONS.. | 240 |
| 3. ACCELERATED AGING..... | 241 |
| SUMMARY..... | 241 |
| OBJECTIVES..... | 241 |
| EQUIPMENT AND PROCEDURE..... | 241 |
| FEEDSTOCK..... | 242 |
| RESULTS..... | 242 |

TABLE OF CONTENTS (CONT'D)

| <u>SECTION</u> | | <u>PAGE</u> |
|----------------|-----------------------------------|-------------|
| | DISCUSSION..... | 244 |
| | RECOMMENDATIONS AND CONCLUSIONS.. | 244 |
| IX | AROMATIC SATURATION..... | 246 |
| | SUMMARY..... | 246 |
| | OBJECTIVES..... | 246 |
| | EQUIPMENT..... | 246 |
| | FEEDSTOCKS..... | 247 |
| | PROCEDURE..... | 247 |
| | RESULTS..... | 248 |
| | DISCUSSION..... | 250 |
| | CONCLUSIONS..... | 255 |

LIST OF FIGURES

| <u>FIGURES</u> | | <u>PAGE</u> |
|----------------|---|-------------|
| II-1 | PODBIELNIAK (I) AND HEMPEL (II) FRACTIONATION OF OCCIDENTAL CRUDE SHAILE OIL | 9 |
| II-2 | API GRAVITY AS A FUNCTION OF BOILING RANGE FOR CRUDE OCCIDENTAL SHAILE OIL.... | 10 |
| II-3 | SULFUR CONTENT AS A FUNCTION OF BOILING RANGE FOR CRUDE OCCIDENTAL SHAILE OIL.... | 11 |
| II-4 | NITROGEN CONTENT AS A FUNCTION OF BOILING RANGE FOR CRUDE OCCIDENTAL SHAILE OIL.... | 12 |
| II-5 | BASIC NITROGEN CONTENT AS A FUNCTION OF BOILING RANGE FOR CRUDE OCCIDENTAL SHAILE OIL..... | 13 |
| II-6 | ARSENIC CONTENT AS A FUNCTION OF BOILING RANGE FOR CRUDE OCCIDENTAL SHAILE OIL..... | 14 |
| III-1 | CRUDE SHAILE HYDROTREATER CONFIGURATION... | 20 |
| III-2 | TEMPERATURE DEPENDENCE OF DESULFURIZATION AT 2 LHSV COBALT MOLYBDATE CATALYST..... | 60 |
| III-3 | IN SITU SHAILE OIL HYDROTREATING OVER NICKEL MOLYBDATE CATALYST: TEMPERATURE DEPENDENCE OF DESULFURIZATION AT 2 LHSV... | 61 |
| III-4 | TEMPERATURE DEPENDENCE OF DENITROGENATION AT 2 LHSV COBALT MOLYBDATE CATALYST..... | 62 |
| III-5 | IN SITU SHAILE OIL HYDROTREATING OVER NICKEL MOLYBDATE CATALYST: TEMPERATURE DEPENDENCE OF DENITROGENATION AT 2 LHSV... | 63 |
| III-6 | IN SITU SHAILE OIL HYDROTREATING OVER COBALT MOLYBDATE CATALYST..... | 64 |
| III-7 | IN SITU SHAILE OIL HYDROTREATING OVER NICKEL MOLYBDATE CATALYST..... | 65 |
| III-8 | SECOND ORDER SPACE VELOCITY RESPONSE OF DENITROGENATION AT 1000 PSIG PRESSURE OVER COBALT MOLYBDATE CATALYST..... | 66 |
| III-9 | IN SITU SHAILE OIL HYDROTREATING OVER NICKEL MOLYBDATE CATALYST: HYDROGEN CONSUMPTION TRENDS..... | 67 |

LIST OF FIGURES (CONT'D)

| <u>FIGURES</u> | | <u>PAGE</u> |
|----------------|---|-------------|
| III-10 | HETEROATOM REMOVAL STABILITY: CRUDE SHALE OIL HYDROTREATING - SERIES M-11..... | 77 |
| III-11 | HETEROATOM REMOVAL STABILITY: CRUDE SHALE OIL HYDROTREATING - SERIES M-12..... | 78 |
| III-12 | MODIFIED CRUDE SHALE HYDROTREATER FOR 30-DAY RUNS..... | 81 |
| III-13 | CSHT AGING RESULTS FOR IN SITU SHALE OIL - TEMPERATURE, PRESSURE, LHSV, HYDROGEN CONSUMPTION..... | 93 |
| III-14 | CSHT AGING RESULTS FOR IN SITU SHALE OIL - °API, SULFUR, NITROGEN, BASIC NITROGEN..... | 94 |
| IV-1 | MICROACTIVITY TEST CRACKING SAMPLE 11103 WT. % CONVERSION..... | 112 |
| IV-2 | MICROACTIVITY TEST CRACKING SAMPLE 11103 VOL. % RECOVERY..... | 113 |
| IV-3 | MICROACTIVITY TEST CRACKING SAMPLE 11205 WT. % CONVERSION..... | 114 |
| IV-4 | MICROACTIVITY TEST CRACKING SAMPLE 11205 VOL. % RECOVERY..... | 115 |
| IV-5 | MICROACTIVITY TEST CRACKING SAMPLE 11312 WT. % CONVERSION..... | 116 |
| IV-6 | MICROACTIVITY TEST CRACKING SAMPLE 11312 VOL. % RECOVERY..... | 117 |
| IV-7 | MICROACTIVITY TEST CRACKING SAMPLE M-112 WT. % CONVERSION..... | 118 |
| IV-8 | MICROACTIVITY TEST CRACKING SAMPLE M-112 VOL. % RECOVERY..... | 119 |
| IV-9 | MICROACTIVITY TEST CRACKING SAMPLE 12205 WT. % CONVERSION..... | 120 |
| IV-10 | MICROACTIVITY TEST CRACKING SAMPLE 12205 VOL. % RECOVERY..... | 121 |

LIST OF FIGURES (CONT'D)

| <u>FIGURES</u> | | <u>PAGE</u> |
|----------------|--|-------------|
| IV-11 | FCC YIELD MAXIMA DEPENDENCE ON FEEDSTOCK BASIC NITROGEN CONTENT FOR IN SITU SHALE OIL..... | 122 |
| IV-12 | COMPARISON OF NITROGEN DOPED AND THE ANALOGOUS FRESH FEED YIELDS..... | 123 |
| IV-13 | MICROACTIVITY TEST CRACKING SAMPLE M-112 LCO - WT. % CONVERSION..... | 142 |
| IV-14 | MICROACTIVITY TEST CRACKING SAMPLE M-112 LCO - VOL. % RECOVERY..... | 143 |
| V-1 | BATCH EXTRACTION OF BASIC NITROGEN..... | 160 |
| V-2 | RATIO OF HYDROCARBON TO NITROGEN REMOVAL IN BATCH EXTRACTION..... | 161 |
| V-3 | CONTINUOUS COUNTERCURRENT ACID EXTRACTION OF BASIC NITROGEN..... | 162 |
| V-4 | RATIO OF HYDROCARBON TO NITROGEN REMOVAL IN CONTINUOUS COUNTERCURRENT EXTRACTION.... | 163 |
| VI-1 | CYCLE OIL HYDROTREATER CONFIGURATION..... | 173 |
| VI-2 | CYCLE OIL HYDROTREATING - IN SITU SHALE OIL - TEMPERATURE DEPENDENCE OF DESULFURIZATION AT 1 LHSV..... | 179 |
| VI-3 | CYCLE OIL HYDROTREATING - IN SITU SHALE OIL - TEMPERATURE DEPENDENCE OF DENITROGENATION AT 1 LHSV..... | 180 |
| VII-1 | GUARDCASE HYDROTREATER CONFIGURATION..... | 185 |

LIST OF FIGURES (CONT'D)

| <u>FIGURES</u> | | <u>PAGE</u> |
|----------------|---|-------------|
| VIII-1 | EFFECT OF TEMPERATURE ON JP-4 YIELD DURING REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL..... | 217 |
| VIII-2 | EFFECT OF PRESSURE ON JP-4 YIELD DURING REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL..... | 218 |
| VIII-3 | DEPENDENCE OF JP-4 YIELD- AS BOTH WT. % OF LIQUID PRODUCT AND AS WT. % OF FEED - ON PRODUCT AROMATIC CONTENT DURING REFORMING OF PARAFFIN-DOPED JP-7 FUEL..... | 219 |
| VIII-4 | VARIATION OF JP-8 YIELD WITH TEMPERATURE DURING REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL..... | 220 |
| VIII-5 | VARIATION OF JP-8 YIELD WITH PRESSURE DURING REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL..... | 221 |
| VIII-6 | DEPENDENCE OF JP-8 YIELD- AS WT. % OF LIQUID PRODUCT - ON PRODUCT AROMATIC CONTENT DURING REFORMING OF n-PARAFFIN- DOPED JP-7 JET FUEL..... | 222 |
| VIII-7 | DEPENDENCE OF JP-8 YIELD- AS WT. % OF FEED - ON PRODUCT AROMATIC CONTENT DURING REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL..... | 223 |
| VIII-8 | EFFECT OF TEMPERATURE ON PRODUCT FREEZE POINT DURING REFORMING OF n-PARAFFIN- DOPED JP-7 JET FUEL..... | 224 |
| VIII-9 | EFFECT OF PRESSURE ON PRODUCT FREEZE POINT DURING REFORMING OF n-PARAFFIN- DOPED JP-7 JET FUEL..... | 225 |
| VIII-10 | DEPENDENCE OF PRODUCT FREEZE POINT ON PRODUCT AROMATIC CONTENT DURING REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL..... | 226 |
| VIII-11 | EFFECT OF TEMPERATURE ON PRODUCT AROMATIC CONTENT -AS WT. % OF FEED -DURING REFORM- ING OF n-PARAFFIN-DOPED JP-7 JET FUEL..... | 227 |

LIST OF FIGURES (CONT'D)

| <u>FIGURES</u> | | <u>PAGE</u> |
|----------------|--|-------------|
| VIII-12 | EFFECT OF PRESSURE ON PRODUCT AROMATIC CONTENT - AS WT. % OF FEED - DURING REFORM- ING OF n-PARAFFIN-DOPED JP-7 JET FUEL..... | 228 |
| VIII-13 | VARIATION OF JP-4 AND JP-8 YIELD - AS WT. % OF FEED - WITH PRODUCT FREEZE POINT DURING REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL..... | 229 |
| VIII-14 | ACCELERATED AGING RESPONSE OF SAMPLE GC-1 (NORMALIZED DATA)..... | 245 |

LIST OF TABLES

| <u>TABLE</u> | | <u>PAGE</u> |
|--------------|--|-------------|
| II-1 | CRUDE SHALE OIL EVALUATION..... | 7 |
| II-2 | CRUDE SHALE OIL EVALUATION..... | 8 |
| III-1 | FEEDSTOCK PROPERTIES - PARAMETER VARIATION STUDIES - OCCIDENTAL IN SITU SHALE OIL..... | 18 |
| III-2 | SERIES 111 RUN CHRONOLOGY..... | 24 |
| III-3 | SERIES 112 RUN CHRONOLOGY..... | 27 |
| III-4 | SERIES 113 RUN CHRONOLOGY..... | 30 |
| III-5 | SERIES 121 RUN CHRONOLOGY..... | 33 |
| III-6 | SERIES 122 RUN CHRONOLOGY..... | 35 |
| III-7 | SERIES 123 RUN CHRONOLOGY..... | 38 |
| III-8 | PARAMETER VARIATION HYDROTREATING SERIES 111 - OPERATING CONDITIONS/ MATERIAL BALANCE..... | 40 |
| III-9 | PARAMETER VARIATION HYDROTREATING SERIES 111 - PRODUCT PROPERTIES/ HETEROATOM REMOVAL..... | 41 |
| III-10 | PARAMETER VARIATION HYDROTREATING SERIES 112 - OPERATING CONDITIONS/ MATERIAL BALANCE..... | 42 |
| III-11 | PARAMETER VARIATION HYDROTREATING SERIES 112 - PRODUCT PROPERTIES/ HETEROATOM REMOVAL..... | 43 |
| III-12 | PARAMETER VARIATION HYDROTREATING SERIES 113 - OPERATING CONDITIONS/ MATERIAL BALANCE..... | 44 |
| III-13 | PARAMETER VARIATION HYDROTREATING SERIES 113 - PRODUCT PROPERTIES/ HETEROATOM REMOVAL..... | 45 |
| III-14 | PARAMETER VARIATION HYDROTREATING SERIES 121 - OPERATING CONDITIONS/ MATERIAL BALANCE..... | 46 |

LIST OF TABLES (CONT'D)

| <u>TABLE</u> | | <u>PAGE</u> |
|--------------|---|-------------|
| III-15 | PARAMETER VARIATION HYDROTREATING SERIES 121 - PRODUCT PROPERTIES/ HETEROATOM REMOVAL..... | 47 |
| III-16 | PARAMETER VARIATION HYDROTREATING SERIES 122 - OPERATING CONDITIONS/ MATERIAL BALANCE..... | 48 |
| III-17 | PARAMETER VARIATION HYDROTREATING SERIES 122 - PRODUCT PROPERTIES/ HETEROATOM REMOVAL..... | 49 |
| III-18 | PARAMETER VARIATION HYDROTREATING SERIES 123 - OPERATING CONDITIONS/ MATERIAL BALANCE..... | 50 |
| III-19 | PARAMETER VARIATION HYDROTREATING SERIES 123 - PRODUCT PROPERTIES/ HETEROATOM REMOVAL..... | 51 |
| III-20 | PARAMETER VARIATION HYDROTREATING SERIES 111 - HYDROGEN DISTRIBUTION..... | 52 |
| III-21 | PARAMETER VARIATION HYDROTREATING SERIES 112 - HYDROGEN DISTRIBUTION..... | 53 |
| III-22 | PARAMETER VARIATION HYDROTREATING SERIES 113 - HYDROGEN DISTRIBUTION..... | 54 |
| III-23 | PARAMETER VARIATION HYDROTREATING SERIES 121 - HYDROGEN DISTRIBUTION..... | 55 |
| III-24 | PARAMETER VARIATION HYDROTREATING SERIES 122 - HYDROGEN DISTRIBUTION..... | 56 |
| III-25 | PARAMETER VARIATION HYDROTREATING SERIES 123 - HYDROGEN DISTRIBUTION..... | 57 |
| III-26 | M-SERIES HYDROTREATING FEED PROPERTIES OF OCCIDENTAL IN SITU SHALE OIL..... | 71 |
| III-27 | CRUDE SHALE OIL HYDROTREATING SERIES M-11 OPERATING CONDITIONS, MATERIAL BALANCE, PRODUCT PROPERTIES..... | 72 |
| III-28 | CRUDE SHALE OIL HYDROTREATING SERIES M-11 PRODUCT FRACTIONATION - M-111..... | 73 |

LIST OF TABLES (CONT'D)

| <u>TABLE</u> | | <u>PAGE</u> |
|--------------|---|-------------|
| III-29 | CRUDE SHALE OIL HYDROTREATING SERIES M-11 PRODUCT FRACTIONATION - M-112..... | 74 |
| III-30 | CRUDE SHALE OIL HYDROTREATING SERIES M-12 OPERATING CONDITIONS, MATERIAL BALANCE, PRODUCT PROPERTIES..... | 75 |
| III-31 | CRUDE SHALE OIL HYDROTREATING SERIES M-12 PRODUCT FRACTIONATION - M-121..... | 76 |
| III-32 | CRUDE SHALE HYDROTREATER AGING OCCIDENTAL CRUDE OIL (06-SH-94-01) FEED PROPERTIES.... | 83 |
| III-33 | CHRONOLOGICAL RUN DESCRIPTION..... | 86 |
| III-34 | OPERATING CONDITIONS, MATERIAL BALANCE..... | 90 |
| III-35 | COMPOSITE PRODUCT INSPECTION, COMPOSITE 3, PERIODS 9-11..... | 95 |
| III-36 | COMPOSITE PRODUCT INSPECTION, COMPOSITE 5, PERIODS 15-20..... | 96 |
| III-37 | COMPOSITE PRODUCT INSPECTION, COMPOSITE 7, PERIODS 25-28..... | 97 |
| III-38 | CATALYST ANALYSIS-IN SITU SHALE OIL HYDROTREATER CATALYST AGING 10/5/79 - 11/2/79..... | 98 |
| IV-1 | MICROACTIVITY TESTS - FRESH FEEDSTOCK..... | 106 |
| IV-2 | MILITARY JET FUEL FROM SHALE OIL PHASE II MAT SUMMARY - FEEDSTOCK 11103..... | 107 |
| IV-3 | MILITARY JET FUEL FROM SHALE OIL PHASE II MAT SUMMARY - FEEDSTOCK 11205..... | 108 |
| IV-4 | MILITARY JET FUEL FROM SHALE OIL PHASE II MAT SUMMARY - FEEDSTOCK 11312..... | 109 |
| IV-5 | MILITARY JET FUEL FROM SHALE OIL PHASE II MAT SUMMARY - FEEDSTOCK M-112..... | 110 |
| IV-6 | MILITARY JET FUEL FROM SHALE OIL PHASE II MAT SUMMARY - FEEDSTOCK 12205..... | 111 |

LIST OF TABLES (CONT'D)

| <u>TABLE</u> | | <u>PAGE</u> |
|--------------|--|-------------|
| IV-7 | FLUID CATALYTIC CRACKING FCR PROCESSING - SAMPLE M-112..... | 129 |
| IV-8 | FLUID CATALYTIC CRACKING FCR PROCESSING - SAMPLE M-121..... | 130 |
| IV-9 | FLUID CATALYTIC CRACKING FCR PROCESSING - SAMPLE OXY-1..... | 134 |
| IV-10 | FLUID CATALYTIC CRACKING FCR PROCESSING - SAMPLE OXY-2..... | 135 |
| IV-11 | FLUID CATALYTIC CRACKING FCR PROCESSING - SAMPLE OXY-3..... | 136 |
| IV-12 | FLUID CATALYTIC CRACKING FCR PROCESSING - SAMPLE OXY-4..... | 137 |
| IV-13 | MILITARY JET FUEL FROM SHALE OIL PHASE II MAT SUMMARY - M-112-LCO..... | 141 |
| V-1 | EXPERIMENTAL DESIGN FOR THE HYDROTREATED IN SITU SHALE OIL DISTILLATE EXTRACTION PARAMETER STUDY..... | 151 |
| V-2 | DATA SUMMARY - PARAMETER STUDY FOR BATCH EXTRACTION OF IN SITU HYDROTREATED SHALE OIL DISTILLATES..... | 152 |
| V-3 | EXTRACTION OF BLENDED PRODUCT - DATA SUMMARY..... | 154 |
| V-4 | CONTINUOUS COUNTERCURRENT EXTRACTION OF SHALE OIL..... | 155 |
| V-5 | M-SERIES CONTINUOUS EXTRACTION RESULTS FOR IN SITU SHALE DISTILLATES..... | 157 |
| V-6 | CONTINUOUS EXTRACTION RESULTS FOR GC-1 STUDY - IN SITU SHALE DISTILLATES..... | 158 |
| V-7 | OPERATING DATA TABLE FOR CONTINUOUS EXTRACTION OF IN SITU SHALE OIL DISTILLATES..... | 165 |
| V-8 | OPERATING PARAMETERS FOR EXTRACTION..... | 168 |

LIST OF TABLES (CONT'D)

| <u>TABLE</u> | | <u>PAGE</u> |
|--------------|--|-------------|
| VI-1 | FEED CHARACTERIZATION: CYCLE OIL HYDROTREATING - SAMPLE M-112..... | 171 |
| VI-2 | FEED CHARACTERIZATION: CYCLE OIL HYDROTREATING - SAMPLE M-121..... | 172 |
| VI-3 | M-SERIES OPERATING CONDITIONS FOR RECYCLE HYDROTREATING OF IN SITU OIL..... | 175 |
| VI-4 | CYCLE OIL HYDROTREATING: IN SITU SHALE OIL..... | 177 |
| VI-5 | DISTILLATION OF FULL RANGE CYCLE OIL HYDROTREATED IN SITU SHALE OIL..... | 181 |
| VII-1 | INITIAL HYDROTREATING..... | 186 |
| VII-2 | REHYDROTREATING..... | 187 |
| VII-3 | INITIAL GUARDCASE HYDROTREATING - SAMPLE M-112..... | 190 |
| VII-4 | REHYDROTREATING OF SAMPLE M-112 THROUGH GUARDCASE HYDROTREATER..... | 191 |
| VII-5 | INITIAL GUARDCASE HYDROTREATING - SAMPLE M-121..... | 192 |
| VII-6 | REHYDROTREATING OF SAMPLE M-121 THROUGH GUARDCASE HYDROTREATER..... | 194 |
| VII-7 | GUARDCASE HYDROTREATING OF SAMPLE GC-1..... | 201 |
| VII-8 | TODD PSEUDOCOMPONENTS - GC-1 FEED..... | 202 |
| VII-9 | TODD PSEUDOCOMPONENTS - GC-1 LINEOUT 1..... | 203 |
| VII-10 | TODD PSEUDOCOMPONENTS - GC-1 LINEOUT 2, 3, 4, 5 AND TEST 1..... | 204 |
| VII-11 | TODD PSEUDOCOMPONENTS - GC-1 ON SPEC..... | 205 |

LIST OF TABLES (CONT'D)

| <u>TABLE</u> | | <u>PAGE</u> |
|--------------|--|-------------|
| VIII-1 | FREEZE POINT MODIFICATION SIMULATION - FEEDSTOCK PROPERTIES..... | 211 |
| VIII-2 | REFORMING OF CETANE..... | 213 |
| VIII-3 | REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL..... | 214 |
| VIII-4 | REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL..... | 215 |
| VIII-5 | REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL..... | 216 |
| VIII-6 | REFORMING OF JET FUEL CONTAINING n-PARAFFIN..... | 231 |
| VIII-7 | REFORMING OF JET FUEL CONTAINING n-PARAFFIN..... | 232 |
| VIII-8 | MILITARY JET FUEL FROM SHALE OIL SAMPLE PREPARATION SEQUENCE..... | 238 |
| VIII-9 | M-SERIES FREZE POINT MODIFICATION..... | 239 |
| VIII-10 | GC-1 ACCELERATED AGING..... | 243 |
| IX-1 | ANALYTICAL RESULTS FOR AROMATIC SATURATED PRODUCTS..... | 249 |
| IX-2 | MATERIAL BALANCE RESULTS FOR AROMATIC SATURATION OF SAMPLE M-112..... | 251 |
| IX-3 | PERTINENT JET FUEL SPECIFICATIONS FOR AROMATIC SATURATE SAMPLES..... | 252 |
| IX-4 | MATERIAL BALANCE RESULTS FOR AROMATIC SATURATION OF SAMPLE M-121..... | 253 |
| IX-5 | MATERIAL BALANCE RESULTS FOR AROMATIC SATURATION OF SAMPLE GC-1..... | 254 |

ABBREVIATIONS

| | |
|---|--|
| A | Aromatics |
| Acid Str | Acid Strength |
| APL | Aero Propulsion Laboratory |
| AFWAL | Air Force Wright Aeronautical Laboratories |
| API | American Petroleum Institute |
| AQ | Aqueous |
| AR SAT | Aromatic Saturation Unit |
| As | Arsenic |
| ASTM | American Society for Testing Materials |
| | |
| bbl | Barrel |
| BN | Basic Nitrogen |
| $\frac{(BN)}{(TN)_p}$ $\frac{(BN)}{(TN)_f}$ | Ratio of Basic Nitrogen over Total Nitrogen in Product to Basic Nitrogen over Total Nitrogen in Feed |
| BPD | Barrels per Day |
| BR NO. | Bromine Number |
| BS&W | Bottoms, Sediment and Water |
| BTU | British Thermal Unit |
| | |
| °C | Degrees Celsius |
| C | Carbon or Heteroatom Concentration |
| C ₁ | Methane |
| C ₂ | Ethane |
| C ₃ | Propane |
| C ₃ ^m | Propylene |

ABBREVIATIONS (CONT'D)

| | |
|-----------------------------|---|
| n-C ₄ | Normal Butane |
| i-C ₄ | Isobutane |
| C ₄ ⁼ | Butylene |
| C ₅ | Pentane |
| C ₅ 's | Pentane and Pentenes |
| C ₅ ⁺ | Compounds Heavier than Pentane in Gas Streams |
| C ₆ | Hexane |
| C/H | Carbon to Hydrogen Ratio |
| cc | Cubic Centimeters |
| cm | Centimeter |
| CO | Carbon Monoxide or Cycle Oil |
| C/O | Catalyst-to-Oil Ratio |
| COHT | Cycle Oil Hydrotreater |
| Co/Mo or CoMo | Cobalt Molybdate Catalyst |
| Cont. Time | Contact Time |
| Conv. | Conversion |
| CR | Cracked |
| CSHT | Crude Shale Hydrotreater |
| cSt | Centistoke |
| CW | Cooling Water |
| E | Activation Energy |
| EP | End Point in a Distillation |
| EQ. SUPER DX | Equilibrium Super DX - a cracking catalyst |

ABBREVIATIONS (CONT'D)

| | |
|---|--|
| EXTD | Extracted |
| °F | Degrees Fahrenheit |
| FCC | Fluid Catalytic Cracker |
| FCR | Fluid Catalytic Reactor |
| Fe | Iron |
| FI | Flow Indicator |
| FIA | Fluorescent Indicator Adsorption - Test Method to Determine Hydrocarbon Types |
| g | Gram |
| GC | Guardcase Hydrotreater |
| GC-1 | Guardcase Study on In Situ Shale Oil |
| Gms | Grams |
| H ₂ | Hydrogen |
| HC | Hydrocarbon |
| HC/N | Ratio of Hydrocarbons to Nitrogen |
| Hg | Mercury |
| Hr or hr | Hours |
| Hr ⁻¹ or hr ⁻¹ | Inverse Hours |
| H ₂ S | Hydrogen Sulfide |
| Hydrog. | Hydrogenated |

ABBREVIATIONS (CONT'D)

| | |
|------------|---|
| IBP | Initial Boiling Point |
| I.D. | Inside Diameter |
| in | Inches |
| JP-4 | Military Specification MIL-T-5624K Turbine Fuel |
| JP-5 | Military Specification MIL-T-5624H Turbine Fuel |
| JP-7 | Military Specification MIL-T-38219 Turbine Fuel |
| JP-8 | Military Specification MIL-T-83133 Turbine Fuel |
| K_0 | Rate Constant |
| lb | Pound |
| LCO | Light Cycle Oil |
| LHSV | Liquid Hourly Space Velocity |
| LPG | Liquefied Petroleum Gas |
| LV% | Liquid Volume Percent |
| MAT | Microactivity Test |
| MAV | Maleic Anhydride Value |
| MAX | Maximum |
| mg | Milligram |
| MIN or min | Minimum |
| min | Minute |

ABBREVIATIONS (CONT'D)

| | |
|----------------------------------|---------------------------------------|
| ml | Milliliter |
| mm | Millimeter |
| MT'L | Material |
| N | Nitrogen |
| N _o or N _f | Nitrogen in Feed |
| N _p | Nitrogen in Product |
| Na ⁺ | Sodium Ion |
| Na ₂ CO ₃ | Sodium Carbonate |
| NaOH | Sodium Hydroxide |
| NH ₃ | Ammonia |
| Ni | Nickel |
| Ni/Mo or NiMo | Nickel Molybdate Catalyst |
| NO. | Number |
| NO _x | Oxides of Nitrogen |
| n-PARAFFIN | Normal Paraffin |
| O | Olefins |
| ON SPEC | Meeting Specifications |
| OXY | Test Series on In Situ Shale Oil |
| P | Pressure |
| (P + N) | Paraffins and Naphthenes |
| PHO | Test Series on Above Ground Shale Oil |

ABBREVIATIONS (CONT'D)

| | |
|-------------------|---|
| PI | Pressure Indicator |
| PID Controller | Proportional-Integral-Derivative Controller |
| ppb | Parts per Billion |
| ppm | Parts per Million |
| psia | Pounds of Force per Square Inch Absolute |
| PSIG or psig | Pounds of Force per Square Inch Gauge |
| Pt/Al | Platinum/Aluminum Catalyst |
| Pt/Re | Platinum/Rhenium Catalyst |
| PV | Parameter Variation |
| | |
| R | Gas Constant |
| °R | Degrees Rankine |
| RAFF | Raffinate |
| RAMS C | Ramsbottom Carbon |
| RCVY | Recovery |
| R&D | Research & Development |
| REF | Reformer |
| REGEN | Regenerator Section of FCC |
| RVP | Reid Vapor Pressure |
| | |
| S | Sulfur |
| SAT | Saturates |
| SCFB | Standard Cubic Feet per Barrel |
| SCFH | Standard Cubic Feet per Hour |
| SIM-D | Simulated Distillation |

ABBREVIATIONS (CONT'D)

| | |
|-----------------------|--------------------------------------|
| SR | Straight Run |
| SS | Stainless Steel |
| SU or SUS | Saybolt Universal Seconds |
| TBP | True Boiling Point |
| TEMP or t | Temperature |
| TIC | Temperature Indicator and Controller |
| V | Vanadium |
| VIS | Viscosity |
| VOL | Volume |
| VOL % | Volume Percent |
| WBS | Work Breakdown Structure |
| WHSV | Weight Hourly Space Velocity |
| WT | Weight |
| WT %, % W, or % WT | Weight Percent |

SYMBOLS

| | |
|---|--|
| = | Equals |
| + | Positive, plus, or greater than as in 600°F+ |
| - | Negative, minus, or less than as in -600°F |
| % | Percent |
| > | Greater Than |
| < | Less Than |
| " | Inches |
| # | Number or Pound |
| Δ | Difference |

SUMMARY

A complete EXTRACTACRACKING evaluation sequence has been performed for Occidental in situ shale oil. Extensive tests for hydrotreating, catalytic cracking, extraction and product upgrading were successfully performed. Data from these tests are contained in this volume.

These tests demonstrate that this oil is an acceptable feedstock for EXTRACTACRACKING. Further, specification JP-4 and JP-8 turbine fuels were produced from these materials and provided to the Air Force.

SECTION I
INTRODUCTION

On February 15, 1979, Ashland Petroleum Company Research and Development Department began work under contract F33615-78-C-2080, An Exploratory Research and Development Program Leading to Specifications for Aviation Turbine Fuel from Whole Crude Shale Oil. This program, funded by the Department of Defense, is designed to evaluate the EXTRACTACRACKING process as a potential improvement in shale oil refining technology.

EXTRACTACRACKING is a novel, integrated process developed by Ashland Petroleum Research and composed of a proprietary combination of hydrotreating, fluid cracking, extraction and product upgrading sequences. The process is designed to reduce costs by minimizing hydrogen consumption and operating severity requirements. A more detailed discussion of the process is contained in Volume I of this report.

Phase I of this study was performed as a preliminary economic analysis of the process and was completed on June 15, 1979. Phase II was performed to evaluate process parameters in order to define optimum operating regions based on cost and to prepare five 500-ml samples of aviation turbine fuel from the complete process. Data obtained during Phase II is reported in three volumes:

Volume I: Preparation of Laboratory-Scale Fuel Samples

Volume II: In Situ Shale Oil Process Data

Volume III: Above-Ground Shale Oil Process Data

This volume collects all data obtained during processing of in situ shale oil during Phase II, for the period June 15, 1979 through October 1, 1980.

Work in Phase II was broken into major functional areas for completion. Since EXTRACTACKING is an integrated process, both screening and sample production studies for further processing were required. Where possible, the program was defined such that small sample quantities could be utilized.

Initial rapid parameter screening tests were performed for the crude shale hydrotreater module. These tests comprised a wide range of operating severities over two catalyst types. Products from these screening tests were fractionated and selected bottoms samples evaluated for FCC performance on the microactivity unit (MAT). Selected distillate samples were processed by batch extraction.

Results from this preliminary screening were utilized to define anticipated required operating severities for these units. Those conditions were then utilized for production of the M-Series samples which were processed through the entire flow sheet.

The M-Series data, plus the earlier screening data, were utilized to define preliminary optimum operating regions by the process computer model developed during

Phase I. Conditions indicated by that preliminary optimization were then utilized for preparation of the listed Oxy sample, which also was processed through the entire processing sequence.

All data obtained for in situ shale oil is contained in this volume. Very little effort has been made herein to define module interactive or other effects; these will be discussed fully in Volume I. The purpose of this volume is to delineate data bases and procedures for further evaluation.

SECTION II

CRUDE SHALE ANALYSIS

SUMMARY

Two types of shale oils, in situ and above ground retorted, have been characterized by fractionation and subsequent analysis of the fractional products. These efforts were required as outlined for fulfillment of Phase II objectives in the Military Jet Fuels from Shale Oil Program.

The shale oils, Occidental Petroleum's in situ oil produced during Retort #6 and Paraho above-ground retorted oil obtained from the government's Anvil Points facility, were handled identically and simultaneously.

OBJECTIVE

The raw shale oils under investigation were fractionated as described in order to provide a detailed definition of physicochemical properties. This data set becomes the basis for all subsequent observations regarding the effectiveness of EXTRACTACRACKING process modules.

MECHANICAL DESCRIPTION

The fractionation of each oil sample was accomplished in two increments of work. Each sample was first distilled in increments to an endpoint of approximately 600°F, after which the >600°F boiling range liquids were transferred to an alternate apparatus and the distillation was continued.

A Podbielniak Semi-Cal model 3650 fractional distillation apparatus was utilized for the low temperature portion of the fractionation. This column is a completely vacuum-jacketed model packed with .09" x .175" x .175" stainless steel Heli-Pak column internals. The column was operated at both atmospheric and subatmospheric pressures at a 5:1 reflux ratio.

In order to perform the high temperature segment of the characterization, the >600°F liquid was transferred to a modified Hempel apparatus. This consisted of a round bottom distillation flask with thermowell, a liquid dividing still head with warm and cold condensing water capability, product receiver, tilting McLeod manometer and vapor trap. The system was evacuated with a Welch brand mechanically backed diffusion pump.

EXPERIMENTAL

A five gallon sample was removed from Occidental in situ oil drum #06-SH-96-01. The 55 gallon drum was heated for two hours on the high setting of a band-type drum heater wrapped around the lower third of the drum. The drum was then agitated vigorously for approximately one minute and a sample withdrawn through a spigot on the drum cap. No filtration was performed.

About one gallon of the oil sample was then dewatered by centrifugation at 140°F. Samples of the raw dewatered

crude were submitted for analytical evaluation and the remainder of the oil was charged to a 1.18"x 48" Podbielniak fractionating column.

The Podbielniak still was operated at a 5:1 reflux ratio to collect fractions in 100°F increments from the IBP up to 600°F. Both volume and weight measurements of the charge and product were made.

The >600°F residue was transmitted to the Synthetic Oils lab where it was subjected to further fractionation. Equipment limitations precluded fractionation beyond the 600°F limit on the Podbielniak unit without fear of thermal decomposition. An alternate method was devised for this high temperature fractionation by distilling at low pressures (<1mm Hg) and total product take-off on the modified Hempel apparatus described previously. The material was fractionated again in 100°F increments above the 600°F initial point to the temperature at which thermal decomposition was observed. Once again, both weight and volume measurements of the charge and product fractions were made.

Samples of each discrete fraction were subjected to analysis as shown in Table II-2.

EXPERIMENTAL RESULTS

Raw analytical results are shown in Tables II-1 and II-2. Fractionation documentation can be found in Figure II-1. Properties of each discrete fraction are displayed graphically in Figures II-2 through II-6.

TABLE II-1

CRUDE SHALE OIL EVALUATION

SAMPLE TYPE: OCCIDENTAL IN SITU CRUDE SHALE OIL

SAMPLE NUMBER: 06-SH-96-01

| ITEM | | ITEM | |
|-------------------------------|-------|---------------------------------|--------|
| CARBON, WT % | 85.9 | GRAVITY, °API | 23.6 |
| HYDROGEN, WT % | 11.0 | SPECIFIC GRAVITY | 0.9123 |
| NITROGEN, WT % | 1.42 | VIS at 100°F, SU | 161.8 |
| SULFUR, WT % | 0.53 | VIS at 140°F, SU | 75.1 |
| OXYGEN, WT % | 1.21 | K FACTOR | 11.6 |
| BASIC NITROGEN, WT % | 0.859 | REID VAPOR PRESSURE | 0.6 |
| PHENOLS, WT % | 0.578 | DISSOLVED H ₂ S, ppm | 21 |
| IRON, ppm | 32 | RAMSBOTTOM CARBON | 1.22 |
| NICKEL, ppm | 11 | SALT, #/1000 bbl | 2.47 |
| VANADIUM, ppm | <1 | BS & W, Vol % | 0.1 |
| ARSENIC, ppm | 24 | ACID NUMBER | 1.36 |
| ORGANIC CHLORIDE, ppm | 4 | POUR POINT, °F | 65 |
| COLOR | 8+ | MALEIC ANHYDRIDE VALUE | 67.4 |
| RECOVERY ON DEWATERING, Vol % | 99.7 | | |

TABLE II-2

CRUDE SHALE OIL EVALUATION

SAMPLE TYPE:

OCCIDENTAL IN SITU

SAMPLE NUMBER: 06-SH-96-01

| ITEM / FRACTION | (278)- 300 | 300- 400 | 400- 500 | 500- 600 | 600+ 700 | 700- 800 | 800- 900 | 900+ |
|-----------------------|---------------|-------------|-------------|-------------|-------------|-------------|-------------|-------|
| Yield, LV % | 0.5 | 3.2 | 12.5 | 17.0 | 66.2 | 5.8 | 23.1 | 28.4 |
| Yield, Wt % | 0.4 | 2.9 | 11.7 | 16.3 | 68.0 | 5.8 | 23.3 | 29.8 |
| K Factor | - | 11.6 | 11.7 | 11.6 | 11.6 | 11.4 | 11.7 | - |
| API Gravity | - | 40.7 | 34.0 | 29.9 | 19.7 | 24.6 | 22.9 | 17.1 |
| Specific Gravity | - | .8217 | .8550 | .8767 | .9358 | .9065 | .9147 | .9522 |
| Carbon, Wt % | - | - | - | - | 85.0 | 86.1 | 84.6 | 85.03 |
| Hydrogen, Wt % | - | - | 12.06 | 11.1 | 11.5 | 12.2 | 11.9 | 11.09 |
| Nitrogen, Wt % | 0.87 | 1.04 | 1.01 | 1.29 | 1.49 | 1.58 | 1.76 | 1.54 |
| Basic Nitrogen, Wt % | - | 0.83 | 0.91 | 0.87 | 0.84 | 0.74 | 0.81 | 0.71 |
| Sulfur, Wt % | - | 0.80 | 0.57 | 0.60 | 0.55 | 0.47 | 0.43 | 0.49 |
| Oxygen, Wt % | - | - | - | - | - | - | - | - |
| Phenols, Wt % | - | 3.12 | - | - | - | - | - | - |
| Iron, ppm | - | - | - | - | - | - | - | - |
| Nickel, ppm | - | - | - | - | - | 2 | <1 | 111 |
| Vanadium, ppm | - | - | - | - | - | <1 | <1 | 23 |
| Arsenic, ppm | - | - | - | - | - | <1 | <1 | 2 |
| Organic Cl, ppm | - | - | 4 | .5 | - | 16 | 19 | 40 |
| Ramsbottom Carbon | - | - | - | - | - | - | - | - |
| Saturates, Vol % | - | - | 31.8 | - | 1.94 | 0.31 | 0.35 | 0.40 |
| Olefins, Vol % | - | - | 32.9 | - | - | - | - | - |
| Aromatics, Vol % | - | - | 35.3 | - | - | - | - | - |
| Pour Point, °F | - | - | - | - | - | 35 | 55 | 95 |
| Viscosity, 60°F, SUS | - | - | - | - | - | - | - | - |
| Viscosity, 100°F, SUS | - | 1.24 | 4.95 | 4.9 | 80.1 | 10.52 | 21.02 | 72.20 |
| Viscosity, 210°F, SUS | - | 0.86 | 1.06 | 1.74 | 15.45 | 2.35 | 3.41 | 6.74 |

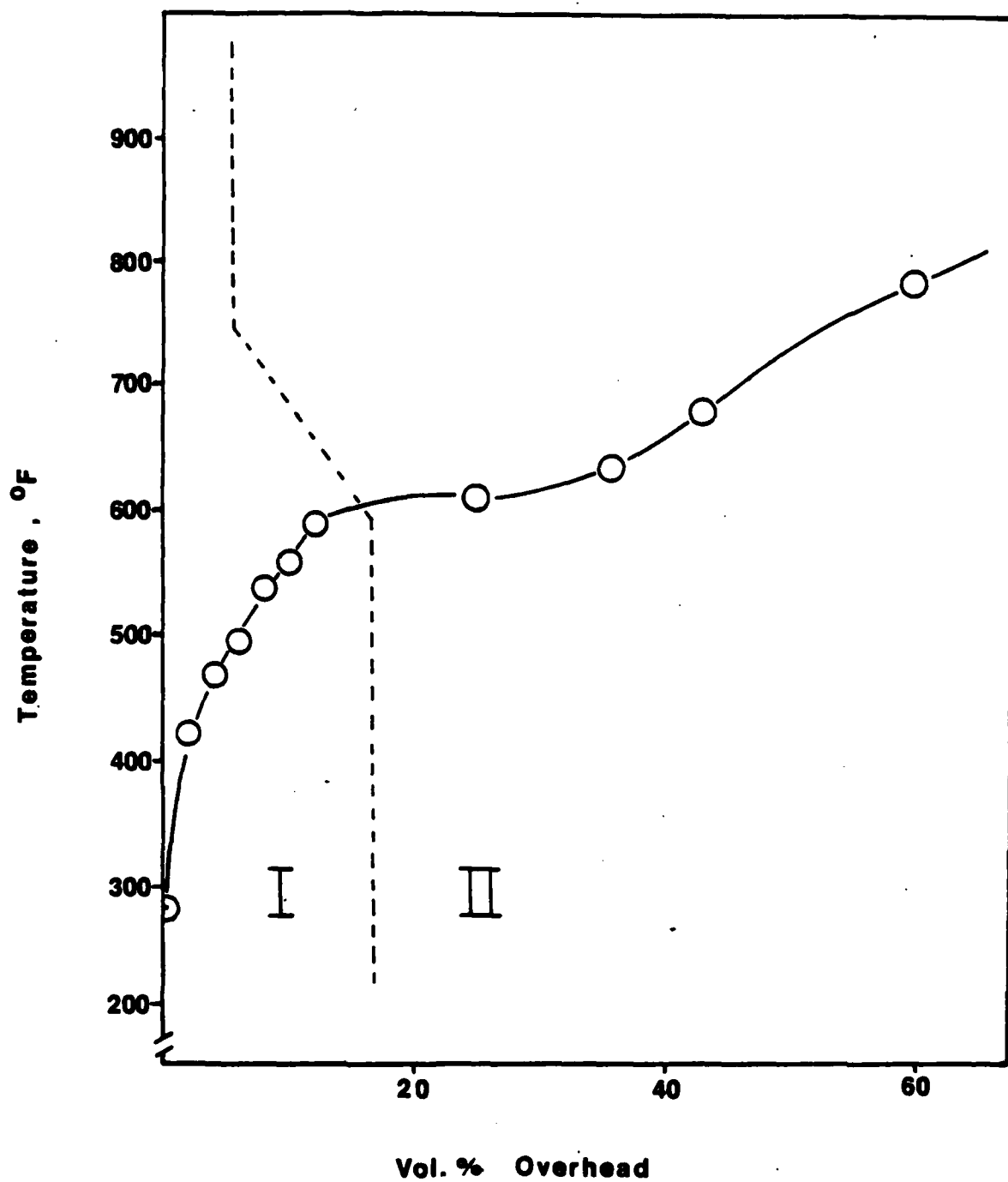


Figure II-1. Podbielniak (I) And Hempel (II) Fractionation Of Occidental Crude Shale Oil

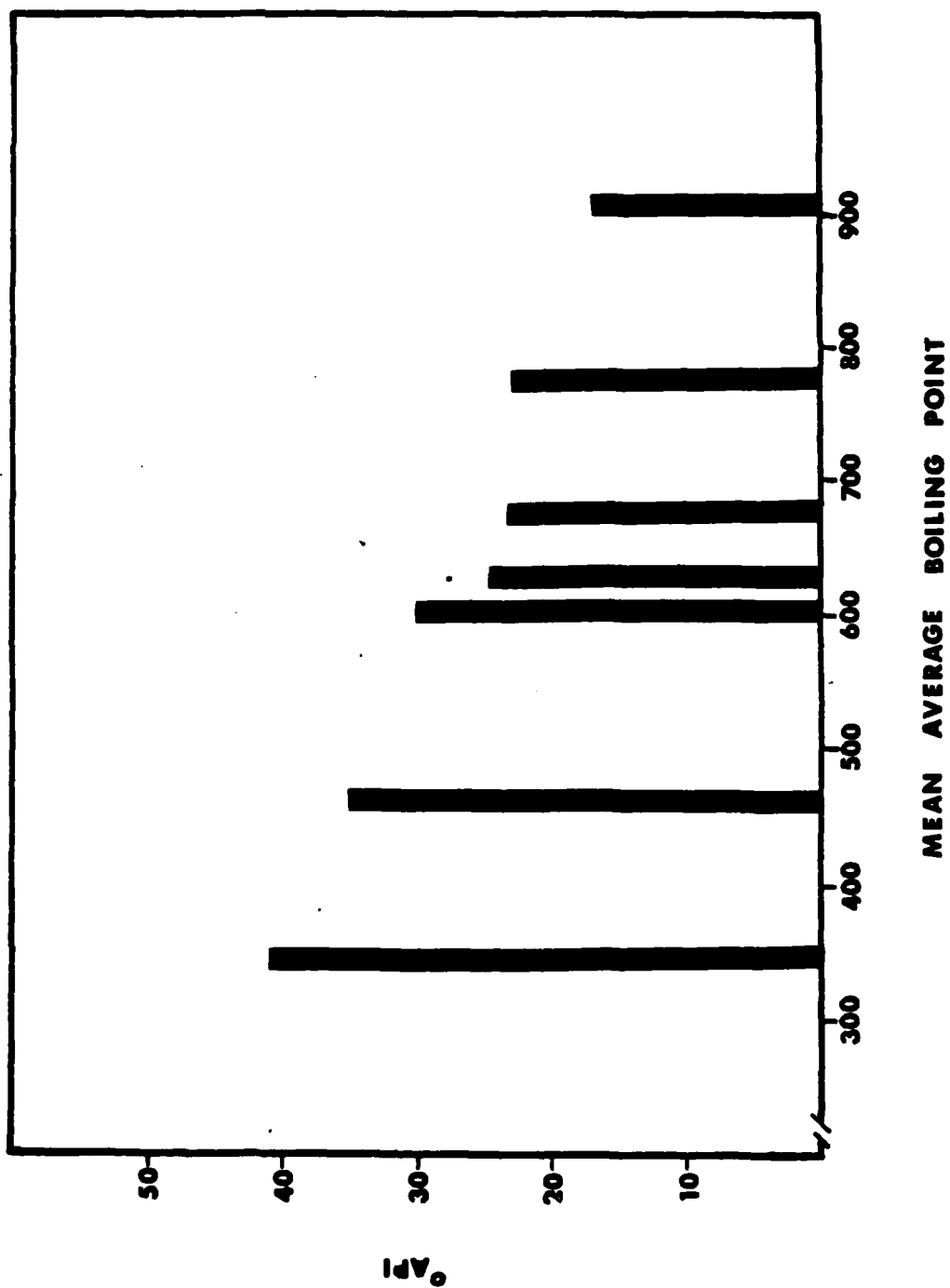


Figure II-2. API Gravity As A Function Of Boiling Range For Crude Occidental Shale Oil

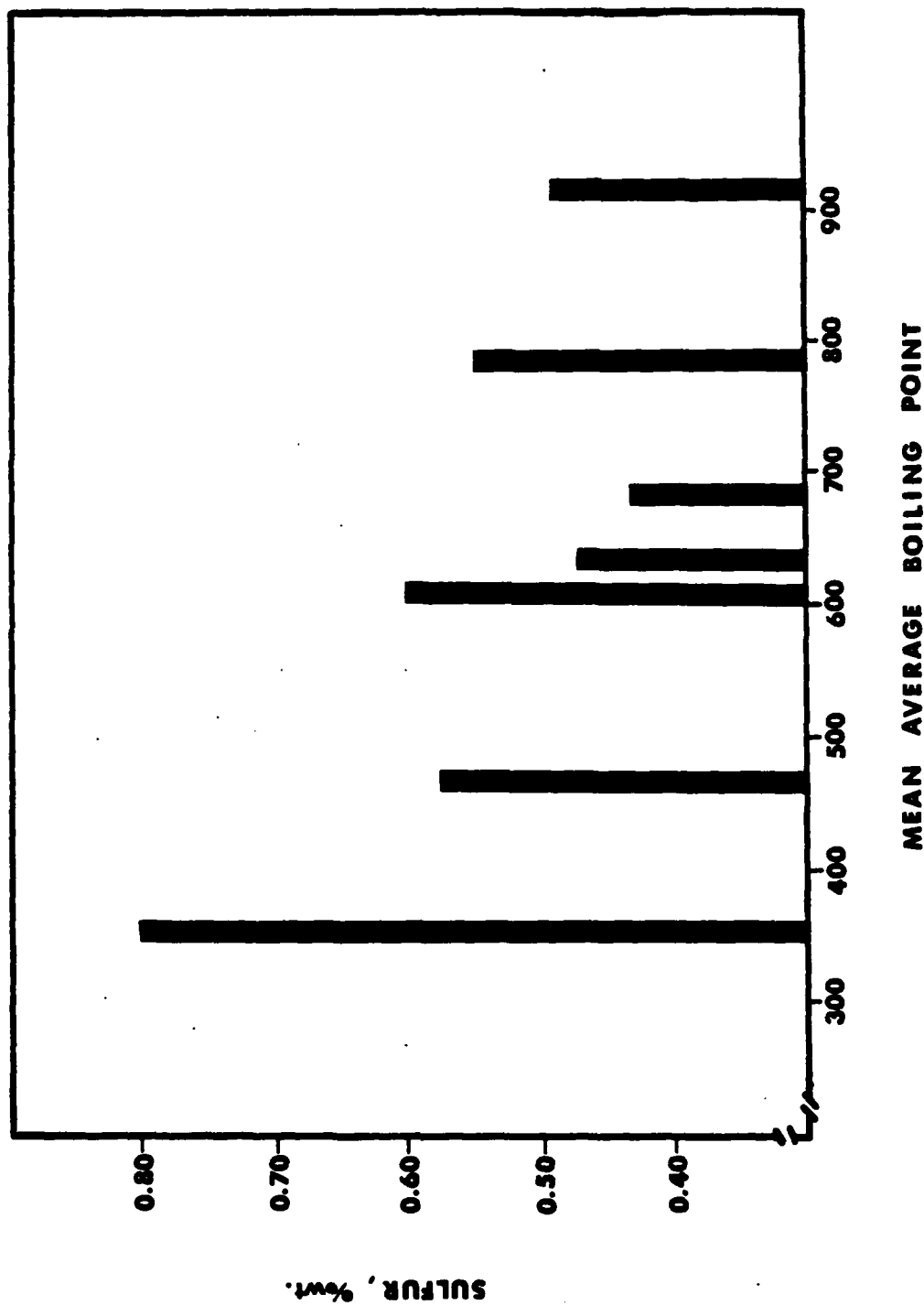


Figure II-3. Sulfur Content As A Function Of Boiling Range For Crude Occidental Shale Oil

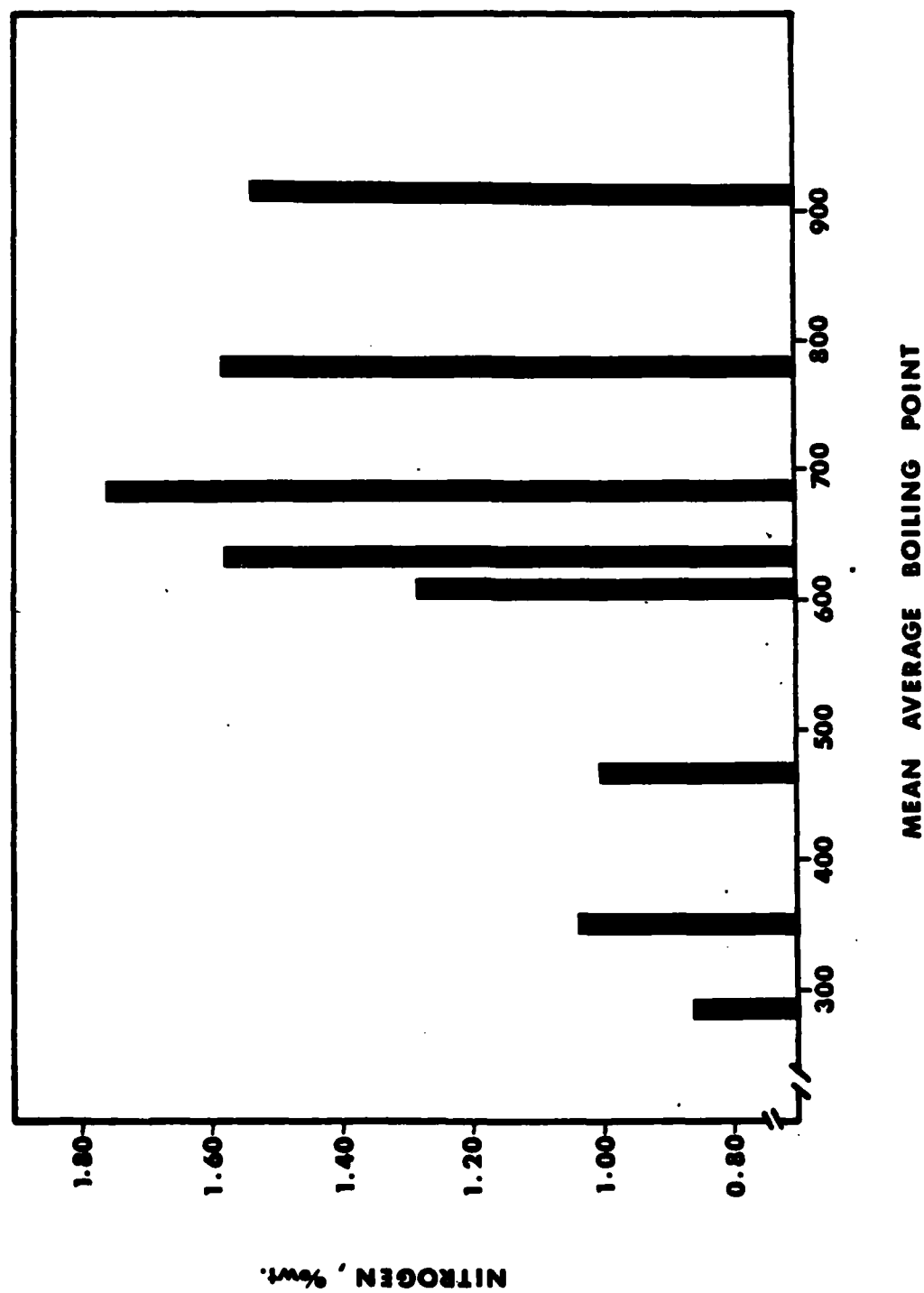


Figure II-4. Nitrogen Content As A Function Of Boiling Range For Crude Occidental Shale Oil

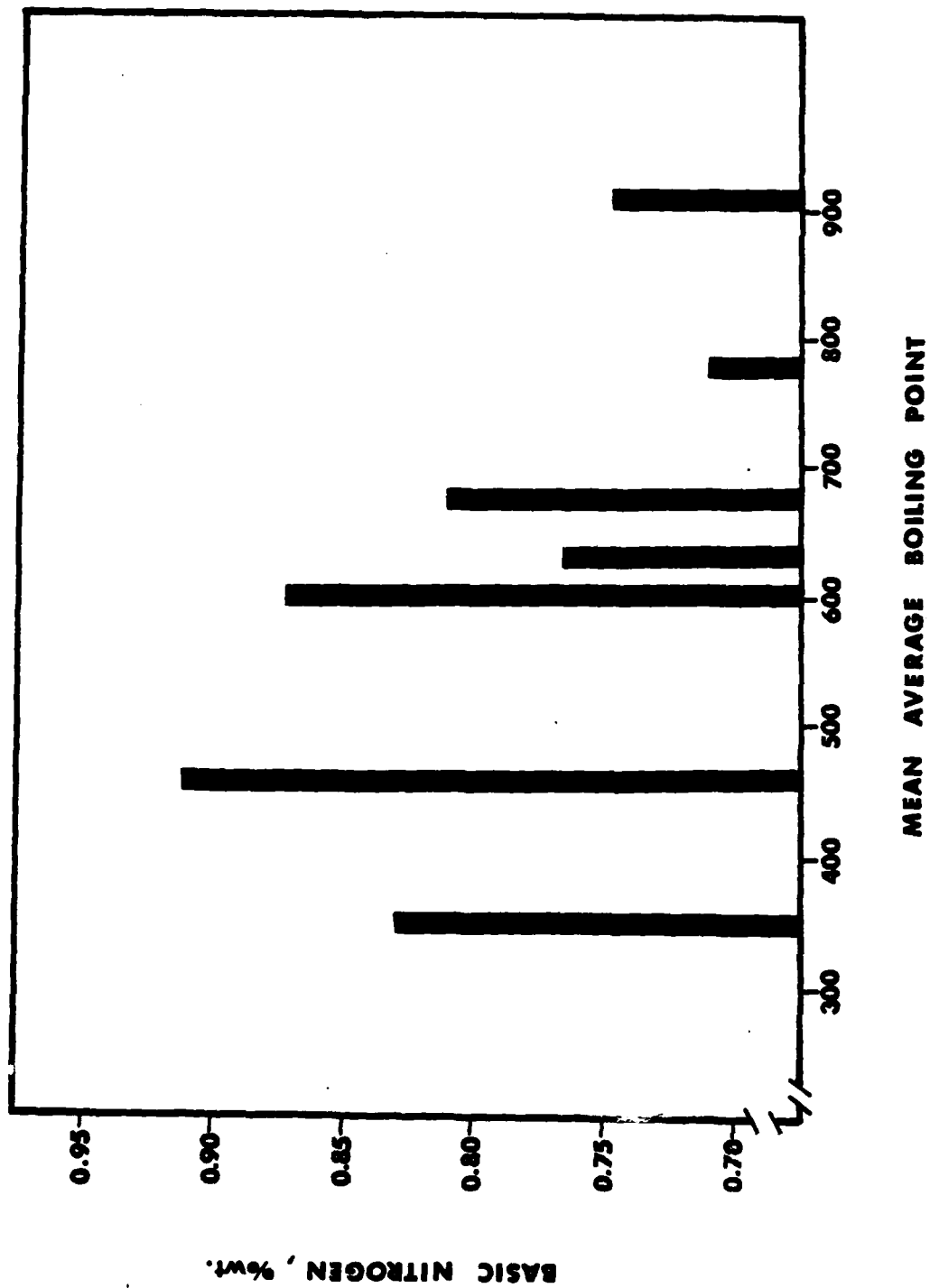


Figure II-5. Basic Nitrogen Content As A Function Of Boiling Range For Crude Occidental Shale Oil

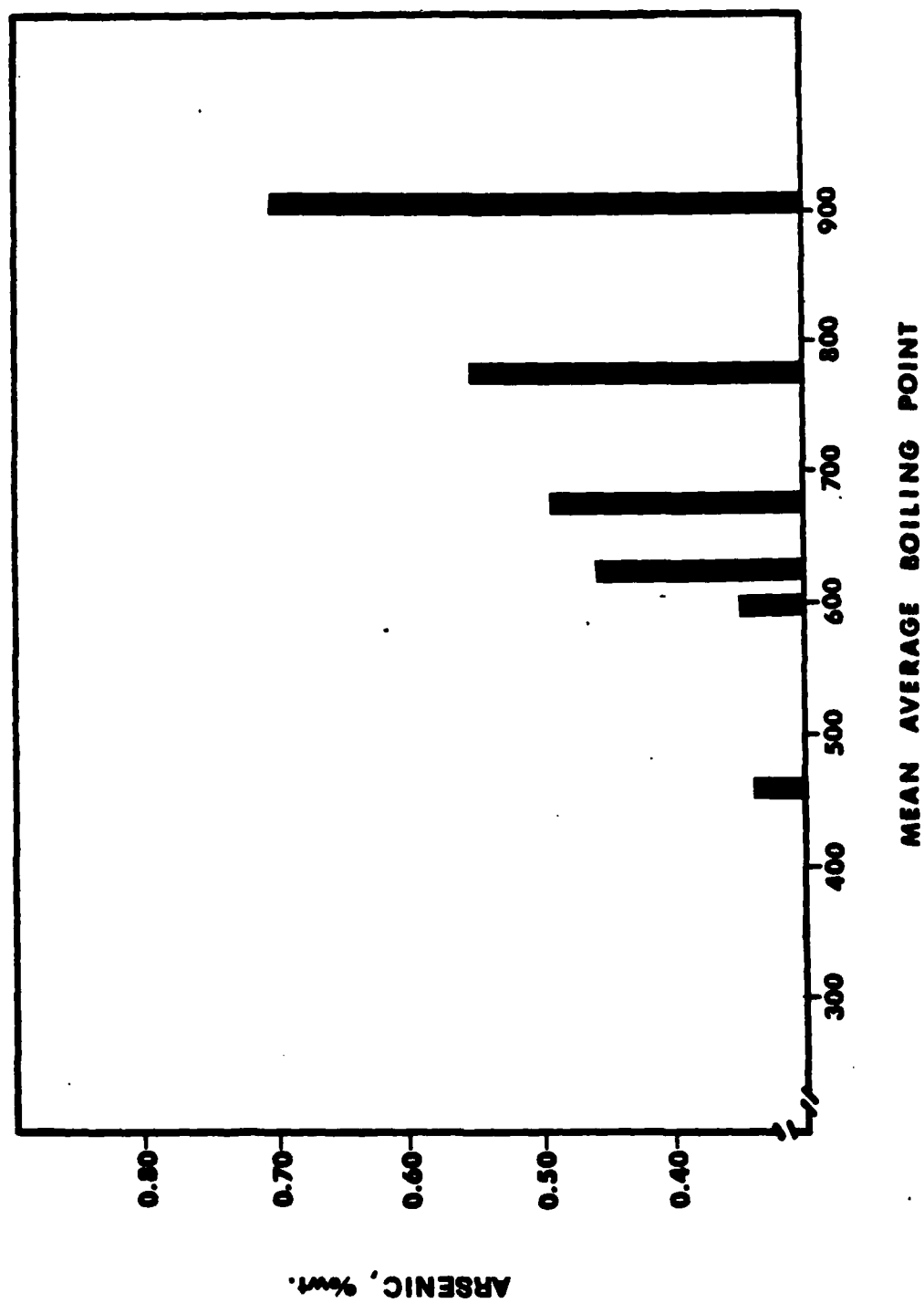


Figure II-6. Arsenic Content As A Function Of Boiling Range For Crude Occidental Shale Oil

DISCUSSION

Boiling ranges quoted for the fractions above 600°F are nominal ranges. This is due mainly to the fractionating efficiency sacrificed with the previously described apparatus in order to maintain low system pressures and temperatures, as well as short column residence time to avoid thermal cracking.

While the majority of the analytical functions were performed within the Research Department, some analyses were performed by independent analysts due to internal equipment limitations. Quantities of certain distillate fractions produced limited the number of analyses which could be performed on those fractions (e.g., IBP-300°F, 300-400°F).

The Watson characterization factor, K , for each of the fractions was derived from correlations using viscosity and API gravity.

CONCLUSIONS

The Occidental crude oil has been successfully separated into the nominal boiling ranges shown in Table II-2. Considerable effort was expended to avoid thermal cracking, a phenomenon more likely observed at lower temperatures for shale oils than for most petroleum crudes.

SECTION III
CRUDE SHALE OIL HYDROTREATER

The crude shale hydrotreater provided for the EXTRACT-ACRACKING process supplies the following functions:

1. Desulfurization
2. Demetallization, and in particular, dearsenation
3. Olefin saturation
4. Denitrogenation
5. Deoxygenation

In contrast to most work in this field, this crude shale hydrotreater is intended to be a low severity, low hydrogen consumption unit. It provides feedstock cleanup with respect to items 1-3, with as little denitrogenation as possible. The combination of low hydrogen addition, while removing metallic contaminants and olefins for handling purposes, is projected to provide an ideal combination of feedstock preparation for both extraction and fluid catalytic cracking.

Work in this area was of necessity extensive, particularly for preparation of samples for further processing. The studies performed were:

1. Parameter screening studies, including operating severity and catalyst evaluations,
2. Sample preparation and catalyst stability studies,
3. Extended sample preparation and catalyst aging studies.

These studies ranged from 16 hour tests for the parameter screening studies to over 700 hours for the aging tests.

1. PARAMETER VARIATION STUDIES

SUMMARY

The overall Military Jet Fuels from Shale Oil program provided a broad range of crude shale hydrotreater data with a minimum of experimental time. This was achieved through a series of parameter variation experiments which are detailed herein.

Each discrete test period from this series of experiments was assigned a three digit prefix followed by a two digit test number. This five digit code was used for documentation and sample retention.

Feedstock for experimental series 111, 112, 113, 121, 122 and 123 was Occidental oil produced in Retort #6 provided by the Air Force in a 96 drum shipment. The drum used for run prefix 111 and 112 experiments was assigned Synthetic Oils #06-SH-96-01, while the feed for runs 113, 121, 122 and 123 was taken from drum #06-SH-95-01. Feedstock samples were drawn directly from the drums and were fed to the reactors without filtration. Feed properties are shown in Table III-1.

TABLE III-1
FEEDSTOCK PROPERTIES - PARAMETER
VARIATION STUDIES - OCCIDENTAL
IN SITU SHALE OIL

| | Run | Series | |
|-----------------|-------------|-------------|------------|
| | 111 | 113 | 122 |
| | <u>112</u> | <u>121</u> | <u>123</u> |
| Drum ID | 06-SH-96-01 | 06-SH-95-01 | |
| °API | 23.7 | 23.7 | |
| Sulfur, Wt. % | 0.53 | 0.53 | |
| Nitrogen, Wt. % | 1.42 | 1.40 | |
| Oxygen, Wt. % | 1.21 | 1.20 | |

OBJECTIVE

This series of parameter variation studies was designed to reveal the short term hydrotreating response of full range in situ shale oil under multiple sets of conditions. A by-product of this arrangement was the production of sufficient refined shale oil products for further studies on subsequent process modules.

The primary objectives of the crude shale hydrotreater are:

1. Sulfur removal
2. Arsenic removal
3. Olefin saturation
4. Removal of iron and other catalyst poisoning metals
5. A small degree of nitrogen and oxygen removal
6. An increase in basic/total nitrogen ratio
7. Some aromatic saturation with minimal hydrogen consumption

MECHANICAL DESCRIPTION

Hydrotreatment was performed through a 1" I.D. universal trickle-flow reactor (see Figure III-1 for the specific reactor configuration). After mixing with hydrogen, the oil passes in a downflow manner across consecutive layers of tabular alumina, the hydrotreating catalyst bed and again over alumina before it is discharged into the low pressure liquid collection portion of the system. Product

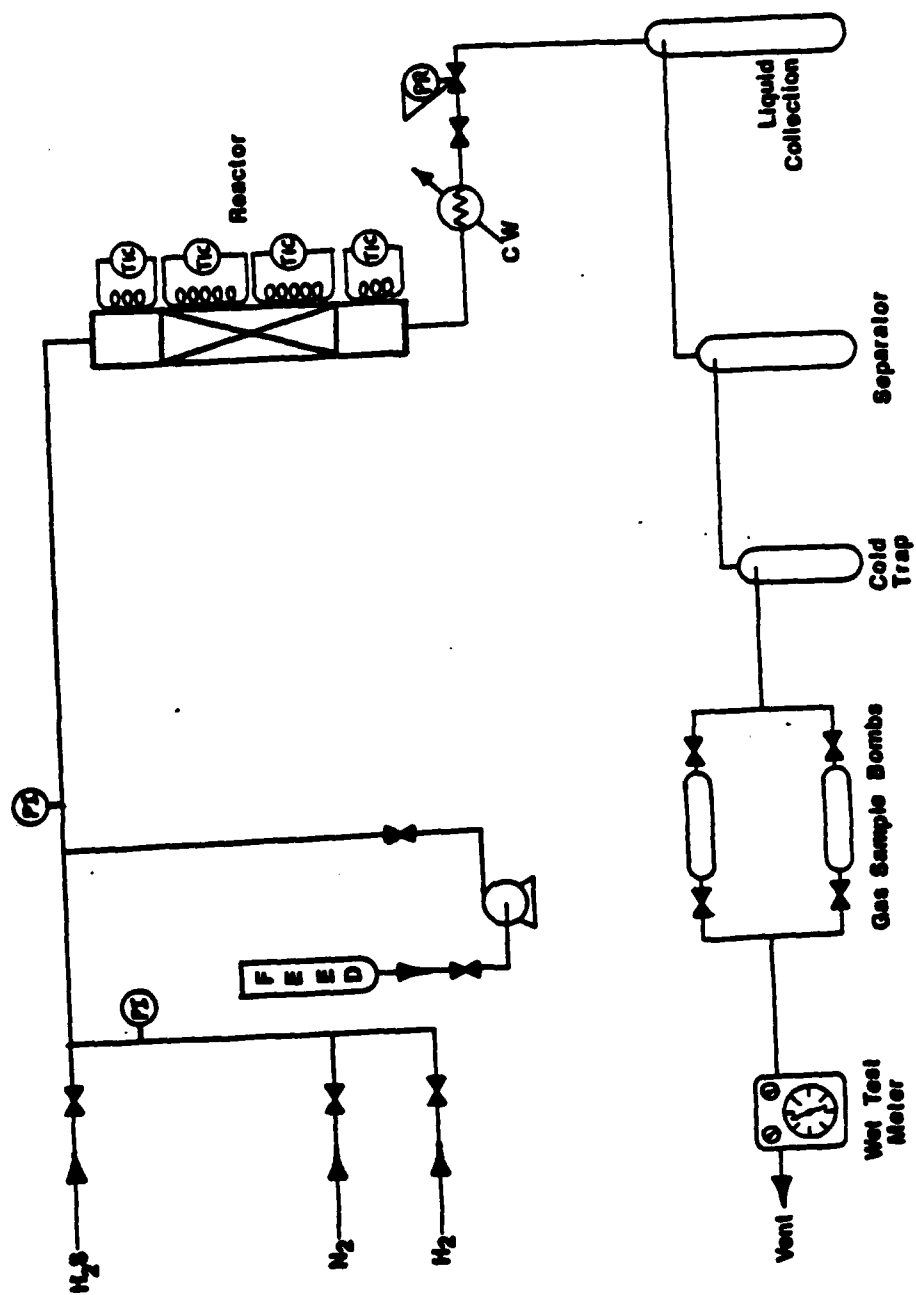


Figure III-1. Crude Shale Hydrotreater Configuration

liquids are collected and weighed while gases are chilled, sampled for analysis and measured through a wet test meter before being vented externally.

CHEMICAL/CATALYST DESCRIPTION

With the exception of the type of commercial hydrotreating catalyst used, reactors were assembled and packed identically for each of the six series of parameter variation studies. Specific descriptions of packing sequences will be given individually for the various experiments. In general, a 100-ml bed of extruded hydrotreating catalyst was mixed in alternating 10-ml increments with an equal volume of sized Ottawa sand and this bed was placed approximately in the center of the universal reactor. As stated previously, the catalyst/sand mixture was "sandwiched" between columns of tabular alumina chips.

Reactors used for treatment of 111, 112 and 113 series experiments were packed with 100-ml of cobalt molybdate commercial hydrotreating catalyst. A nickel molybdate type catalyst was used in series 121, 122 and 123 hydrotreating.

Each fresh charge quantity of catalyst (i.e., each 100-ml) was presulfided in situ with H_2S at maximum run temperature and bottle pressure for two hours.

FEEDSTOCK

Two feedstock drums were utilized for these studies. Properties of these drums are shown in Table III-1, and, as

can readily be seen, these properties are essentially identical.

EXPERIMENTAL

Each run series consisted of 12 discrete tests (e.g., 11101 through 11112). Eight-hour material balance periods were used in order to gather as much data as possible in the shortest period of time. In each series the catalyst was dumped and the reactor recharged between the sixth and seventh tests. Specific operations for each series can be found under each run-prefixed experimental description.

Each discrete test period from this series of experiments was assigned a three-digit prefix followed by a two-digit test number. This five digit code was used for documentation and sample retention.

Prefixes were generated in the form:

XYZ

Where X = Shale Type

1 = In Situ

2 = Above Ground

Where Y = Catalyst Type

1 = Co/Mo

2 = Ni/Mo

Where Z = Pressure

1 = 500 psig

2 = 1000 psig

3 = 2000 psig

Total sample number, for example, for a 500 psig run on in situ oil, over Co/Mo catalyst, at 600°F and 1 LHSV would be: 11101. The in situ oil feed was hydrotreated over the range of conditions shown below:

| | |
|--------------|----------------------|
| Temperature: | 600-750°F |
| LHSV: | 1-4 hr ⁻¹ |
| Pressure: | 500-2000 psig |
| Catalyst: | Ni/Mo, Co/Mo |

EXPERIMENTAL RUN PREFIX 111

Occidental oil from drum 06-SH-96-01 was hydrotreated over Ni/Mo catalyst at 500 psig total pressure and over the ranges 600-750°F and 1-4 LHSV.

The reactor was packed with 100-ml of 1/8" catalyst and 100-ml of Ottawa sand in alternating 10-ml increments, followed by tapping to pack the bed. The postheat alumina rose to a depth 34" from the reactor inlet, a 13" catalyst bed rested on top of the postheat zone, and the remainder of the reactor space was filled with tabular alumina to comprise the preheat zone.

After pressure testing, the catalyst was presulfided with excess H₂S at 750°F and bottle pressure for two hours. The unit was cooled with flowing hydrogen and feed was initiated. Temperatures were raised in 50°F increments every 1/2 hour until the desired operating temperature was achieved.

A chronological run description is shown in Table III-2.

Product from each material balance period was weighed and fractionated into IBP-400, 400-600 and 600°F+ fractions for analysis.

TABLE III-2

SERIES 111 RUN CHRONOLOGY

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|------------------|--|
| 6/22 | | Reactor packed, pressure tested |
| 6/25 | | Catalyst presulfided |
| 6/26 | 0350 | Begin 11101 lineout |
| | 1150 | Begin 11101 test |
| | 1950 | End 11101 test, begin 11102 lineout |
| 6/27 | 0350 | Begin 11102 test |
| | 1150 | End 11102 test, begin 11103 lineout |
| | 1950 | Begin 11103 test |
| | 2055 | H ₂ rate reduced to 10 CFH |
| | 2155 | Feed cans changed, new feed gravity measured |
| | 2455 | Oil in off-gas line; line removed and cleaned |
| 6/28 | 0350 | End 11103 test, begin 11104 lineout |
| | 0615 | Pump failure |
| | 0650 | Replacement pump failed, temperatures lowered 50°F |
| | 0920 | Pump rebuilt and working |
| | 1150 | H ₂ rate corrected, begin 11104 test |
| | 1950 | End 11104 test, begin 11105 lineout |
| | 2150 | H ₂ rate adjusted, begin 11105 test |
| | 2335 | H ₂ rate twice desired rate, adjusted |
| 6/29 | 0550 | End 11105 test, begin 11106 lineout |
| | 0750 | End 11106 lineout, begin test 11106 |
| | 1550 | End 11106 test, unit shutdown |
| 7/3 | | Reactor repacked |
| 7/5 | | Pressure check, presulfiding |
| 7/9 | 1520 | Begin 11107 lineout |
| | 2320 | Begin 11107 test |

TABLE III-2 (CONT'D)

SERIES 111 RUN CHRONOLOGY

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|------------------|---|
| 7/10 | 0720 | End 11107 test, begin 11108 lineout |
| | 1520 | Begin 11108 test |
| | 1820 | Collection vessel stopper off, wet test meter readings off |
| | 2320 | End 11108 test, begin 11109 lineout |
| 7/11 | 0720 | Begin 11109 test |
| | 1520 | End 11109 test, begin 11110 lineout |
| | 1610 | H ₂ rate adjusted |
| | 2320 | Begin 11110 test |
| 7/12 | 0320 | Wet test meter replaced |
| | 0720 | End 11110 test, begin 11111 lineout |
| | 1520 | Begin 11111 test |
| | 1920 | H ₂ rate reduced |
| | 2320 | End 11111 test, begin 11112 lineout |
| 7/13 | 0620 | Wet test meter replaced |
| | 0720 | Begin 11112 test |
| | 1050 | Pump replaced |
| | 1520 | End 11112 test; unit shutdown |

EXPERIMENTAL RUN PREFIX 112

The Occidental oil feed from drum 06-SH-96-01 was hydrotreated over a 100-ml void-filled bed of 1/8" Co/Mo extrudate. System pressure was maintained at 1000 psig while temperatures and space rates were varied from 600-750°F and 1-4 hr⁻¹, respectively.

A bed of tabular alumina rising to within 34.5" of the reactor inlet constituted the postheat zone; on top of this bed rested a 13" catalyst bed void-filled with Ottawa sand, and the remainder of the reactor was filled with tabular alumina as preheat.

After pressure testing, the catalyst was presulfided with H₂S at 775°F and bottle pressure for two hours. The unit was cooled with flowing hydrogen and feed initiated. Temperatures were increased in 50°F increments each 1/2 hour to the desired level.

A chronological run description is shown in Table III-3.

Each material balance product was weighed and fractionated into IBP-400, 400-600 and 600°F+ fractions for analysis.

EXPERIMENTAL RUN PREFIX 113

The Occidental oil feed from drum #06-SH-95-01 was hydrotreated over Co/Mo catalyst at a total system pressure of 2000 psig. Temperatures and space rates were varied over the ranges 600-750°F and 1-4 hr⁻¹, respectively.

TABLE III-3

SERIES 112 RUN CHRONOLOGY

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|------------------|---|
| 6/25 | | Reactor packed, pressure tested, pre-sulfided |
| | 1230 | Feed initiated |
| | 1635 | Problems controlling reactor pressure and feed rate encountered |
| 6/26 | 0130 | Begin 11201 lineout |
| | 0720 | Unit pressure high, adjusted |
| | 0930 | Begin 11201 test |
| | 1730 | End 11201 test, begin 11202 lineout |
| 6/27 | 0025 | Reactor plugged, blown out with pressure |
| | 0130 | Begin 11202 test |
| | 0625 | H ₂ flowmeter malfunction |
| | 0812 | Reactor shutdown |
| | 1550 | Reactor restarted @ 500°F, 50 ml/hr feed, 10 CFH H ₂ |
| 6/28 | 0230 | End 11203 lineout, begin 11203 test |
| | 1030 | End 11203 test, begin 11204 lineout |
| | 1530 | Begin 11204 test |
| | 2330 | End 11204 test, begin 11205 lineout |
| 6/29 | 0130 | End lineout, begin 11205 test |
| | 0930 | End 11205 test, begin 11206 lineout |
| | 1130 | End lineout, begin 11206 test |
| | 1930 | End 11206 test, unit shutdown |
| 7/3 | | Reactor packed |
| 7/5 | | Pressure check |
| 7/6 | | Presulfiding |
| 7/9 | 0440 | Feed initiated |
| | 1640 | Begin 11207 lineout |
| | 2200 | Pump failure |

TABLE III-3 (CONT'D)

SERIES 112 RUN CHRONOLOGY

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|------------------|---|
| 7/10 | 0040 | End lineout, begin 11207 test |
| | 0840 | End 11207 test, begin 11208 lineout |
| | 1640 | End lineout, begin 11208 test |
| 7/11 | 0040 | End 11208 test, begin 11209 lineout |
| | 0840 | End lineout, begin 11209 test |
| | 1640 | End 11209 test, begin 11210 lineout |
| | 1740 | H ₂ rate running low |
| 7/12 | 0040 | End lineout, begin 11210 test |
| | 0840 | End 11210 test, begin 11211 lineout |
| | 1640 | End lineout, begin 11211 test |
| | 1650 | Wet test meter changed |
| 7/13 | 0040 | End 11211 test, begin 11212 lineout |
| | 0840 | End lineout, begin 11212 test |
| | 0940 | Problems with preheat controller, test to be restarted |
| | 2050 | Begin test 11212 |
| 7/14 | 0450 | End 11212 test, reactor shutdown |

The reactor was packed to within 34" of the inlet with tabular alumina as postheat, a 13" bed of 100-ml of void-filled 1/8" Co/Mo catalyst was added, and the remainder of the reactor was filled with tabular alumina to make up the preheat zone.

After pressure testing, the catalyst was presulfided to 800°F at full bottle pressure for one hour. The unit was cooled with flowing hydrogen and feed initiated. Temperatures were increased in 50°F increments each 1/2 hour to the desired level.

A chronological run description is shown in Table III-4.

Each material balance product was weighed and fractionated into IBP-400, 400-600 and 600°F+ fractions for analysis.

EXPERIMENTAL RUN PREFIX 121

This feedstock was hydrotreated over nickel molybdate catalyst at 500 psig total pressure, over a temperature and LHSV range of 600-750°F and 1-4 .hr⁻¹, respectively.

The reactor was packed with 100-ml (85.3g) of 1/8" catalyst and 100-ml of Ottawa sand. A postheat zone of tabular alumina was added to within 34" of the reactor top, followed by catalyst and sand in 10-ml increments to a total length of 12.75", and the remainder packed with tabular alumina as preheat. Following pressure testing, the

TABLE III-4

SERIES 113 RUN CHRONOLOGY

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|--|--|
| 7/31 | | Reactor packed, pressure tested |
| 8/1 | 1045 | Presulfiding Wet test meter replaced |
| 8/2 | 0040 0840 1040 1220 1840 2115 2150 | Begin 11301 lineout Pump failure Pump failure Pump failure End lineout, begin 11301 test Pump failure Pump failure |
| 8/3 | 0340 1140 1940 | Test 11301 restarted after pump situation rectified End 11301 test, begin 11302 lineout End lineout, begin 11302 test |
| 8/4 | 0340 0930 1340 2140 | End 11302 test, begin 11303 lineout Erratic H ₂ rate End lineout, begin 11303 test End 11303 test, begin 11304 lineout |
| 8/5 | 0540 1340 2140 | End lineout, begin 11304 test End 11304 test, begin 11305 lineout End lineout, begin 11305 test |
| 8/6 | 0540 1340 2140 | End 11305 test, begin 11306 lineout End lineout, begin 11306 test End 11306 test, unit shutdown |
| 7/31 | | Reactor packed, pressure tested |
| 8/1 | 2320 | Presulfiding Begin 11307 lineout |
| 8/2 | 0920 1720 | End lineout, begin 11307 test End 11307 test, begin 11308 lineout |

TABLE III-4 (CONT'D)

SERIES 113 RUN CHRONOLOGY

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|------------------|---|
| 8/3 | 0120 | End lineout, begin 11308 test |
| | 0520 | Pump failure |
| | 0615 | Pump failure |
| | 1100 | Feed buret broken, test to be restarted |
| | 2020 | Begin 11308 test |
| 8/4 | 0420 | End 11308 test, begin 11309 lineout |
| | 1220 | End lineout, begin 11309 test |
| | 2020 | End 11309 test, begin 11310 lineout |
| 8/5 | 0420 | End lineout, begin 11310 test |
| | 1220 | End 11310 test, begin 11311 lineout |
| | 2020 | End lineout, begin 11311 test |
| 8/6 | 0420 | End 11311 test, begin 11312 lineout |
| | 1220 | End lineout, begin 11312 test |
| | 2020 | End 11312 test, unit shutdown |

catalyst was presulfided with H_2S at 650°F and bottle pressure for one hour. The unit was cooled to 200°F with flowing hydrogen and feed introduced. Temperatures were raised in 50°F increments every 1/2 hour to 600°F.

A chronological run description is shown in Table III-5.

Each material balance product was weighed and fractionated into IBP-400, 400-600 and 600°F fractions for analysis.

EXPERIMENTAL RUN PREFIX 122

This feedstock was hydrotreated over nickel molybdate catalyst at 1000 psig total pressure, over a temperature and LHSV range of 600-750°F and 1-4 hr^{-1} , respectively.

The reactor was packed with 100-ml (85.3g) of 1/8" catalyst and 100-ml of Ottawa sand. Tabular alumina was charged as postheat to a level 34" from the reactor top, followed by catalyst and sand in 10-ml increments to a total length of 13", and the remainder packed with tabular alumina as preheat. Following pressure testing, the catalyst was presulfided with H_2S at 650°F and bottle pressure for one hour. The unit was cooled to 200°F with flowing hydrogen and feed introduced. Temperatures were raised in 50°F increments every 1/2 hour to 600°F.

A chronological run description is attached as Table III-6.

TABLE III-5

SERIES 121 RUN CHRONOLOGY

| DATE | TIME, HRS | ITEM |
|---------------|-----------|---|
| 7/17 | 0340 | Start lineout |
| | 1240 | Start material balance, 12101 |
| | 2040 | End material balance, 12101; lineout 12102 |
| 7/18 | 0440 | Start material balance, 12102 |
| | 1240 | End material balance, 12102; lineout 12103 |
| | 2040 | Start material balance, 12103 |
| 7/19 | 0440 | End material balance, 12103; start lineout for 12104 |
| | 0750 | Temperature, gas rates low, hydrogen supply low |
| | 0822 | Hydrogen flow lost |
| | 0900 | Hydrogen flow re-established; lineout for 12106 instead of 12104 |
| | 1440 | Start material balance, 12106 |
| | 2240 | End material balance, 12106; lineout 12105 |
| | | |
| 7/20 | 0440 | Pump failed; diaphragm ruptured, some product contamination could have occurred |
| | 0530 | Pump failed |
| | 0710 | Pump failed |
| | 0845 | Pump failed; feed buret changed |
| | 1030 | Pump failed |
| | 1205 | Pump failed |
| | 1640 | Start material balance, 12105 |
| | 2335 | Pump failed |
| | 2440 | End material balance 12105; lineout 12104 |
| | | |
| 7/21 | 0840 | Start material balance, 12104 |
| | 1640 | End material balance, 12104; cool reactor and shut down |
| 7/22- 7/25 | | Reactor repacked with fresh catalyst analogous to initial charge. Presulfiding and start-up procedures same, except pre-sulfided to 750°F |

TABLE III-5 (CONT'D)

SERIES 121 RUN CHRONOLOGY

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|------------------|---|
| 7/26 | 0940 | Start lineout, 12107 |
| | 1740 | Start material balance, 12107 |
| 7/27 | 0140 | End material balance, 12107; lineout 12108 |
| | 0940 | Start material balance 12108 |
| | 1540 | Frozen cold trap causes gas loss |
| | 1740 | End material balance, 12108; lineout 12109 |
| 7/28 | 0140 | Start material balance, 12109 |
| | 0220 | Gas loss |
| | 0940 | End material balance, 12109; lineout 12110 |
| | 1740 | Start material balance 12110 |
| 7/29 | 0140 | End material balance, 12110; lineout 12111 |
| | 0940 | Start material balance, 12111 |
| | 1740 | End material balance, 12111; lineout 12112 |
| 7/30 | 0140 | Start material balance, 12112 |
| | 0940 | End material balance, 12112; unit shut down, cooled and disassembled |

TABLE III-6

SERIES 122 RUN CHRONOLOGY

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|---------------|--|---|
| 7/15 | | Reactor packed, pressure tested |
| 7/16 | 1230 | Presulfiding Feed initiated |
| 7/17 | 0120 0420 0530 0630 0730 1120 1640 1720 | Begin lineout 12201 Pump failure Pump failure Pump failure Pump failure Start material balance 12201 Pump failure cancel material balance Start material balance 12201 |
| 7/18 | 0120 0920 1720 2320 | End material balance 12201; lineout 12202 Start material balance 12202 End material balance 12202; lineout 12203 Product effluent blockage caused product losses |
| 7/19 | 0020 0730 0822 0900 0940 | Start material balance 12203 Product effluent blockage caused product losses Loss of hydrogen flow Hydrogen flow reinitiated End material balance 12203; lineout 12206 |
| 7/20 | 0120 0920 1720 | End material balance 12206; lineout 12205 Start material balance 12205 End material balance 12205; lineout 12204 |
| 7/21 | 0120 0920 | Start material balance 12204 End material balance 12204; shutdown and dump reactor |
| 7/22- 7/23 | | Reactor repacked and pressure tested |
| 7/24- 7/25 | | Presulfide to 750°F |
| 7/25 | 1520 | Feed started |

TABLE III-6 (CONT'D)

SERIES 122 RUN CHRONOLOGY

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|------------------|--|
| 7/26 | 0420 | Start lineout for 12207 |
| | 1220 | Start material balance 12207 |
| | 2020 | End material balance 12207; lineout 12208 |
| 7/27 | 0420 | Start material balance 12208 |
| | 1220 | End material balance 12208; lineout 12209 |
| | 2020 | Start material balance 12209 |
| 7/28 | 0420 | End material balance 12209; lineout 12210 |
| | 1220 | Start material balance 12210 |
| | 2020 | End material balance 12210; lineout 12211 |
| 7/29 | 0420 | Start material balance 12211 |
| | 1220 | End material balance 12211; lineout 12212 |
| | 2020 | Start material balance 12212 |
| 7/30 | 0420 | End material balance 12212, shutdown and dump reactor |

Each material balance product was weighed and fractionated into IBP-400, 400-600 and 600°F fractions for analysis.

EXPERIMENTAL RUN PREFIX 123

This feedstock was hydrotreated over nickel molybdate catalyst at 2000 psig total pressure, over a temperature and LHSV range of 600-750°F and 1-4 hr⁻¹, respectively.

The reactor was packed with 100-ml (85.3g) of 1/8" catalyst and 100-ml of Ottawa sand. First tabular alumina was charged as postheat until the top of this zone measured 34" from the reactor inlet. Then catalyst and sand were added in 10-ml increments to a total length of 13.25", and the remainder of the reactor packed with tabular alumina as preheat. Following pressure testing, the catalyst was pre-sulfided with H₂S at 650°F and bottle pressure for one hour. The unit was cooled to 200°F with flowing hydrogen and feed introduced. Temperatures were raised in 50°F increments every 1/2 hour to 600°F.

A chronological run description is attached as Table III-7.

Each material balance product was stabilized, but no fractionations were performed on these materials.

EXPERIMENTAL RESULTS

The full data results are presented in Tables III-8 through III-25.

TABLE III-7

SERIES 123 RUN CHRONOLOGY

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|------------------|---|
| 8/23 | | Pack reactor, pressure test |
| 8/24 | | Presulfide to 650°F |
| 8/27 | 1200 | Feed initiated |
| | 1250 | Pump failure |
| | 1920 | Start lineout 12301 |
| 8/28 | 0320 | Start material balance 12301 |
| | 1120 | End material balance 12301; lineout 12302 |
| | 1920 | Start material balance 12302 |
| 8/29 | 0320 | End material balance 12302; lineout 12303 |
| | 0920 | Change wet test meter - low water level |
| | 1120 | Start material balance 12303 |
| | 1920 | End material balance 12303; lineout 12304 |
| 8/30 | 0320 | Start material balance 12304 |
| | 1120 | End material balance 12304; lineout 12305 |
| | 1920 | Start material balance 12305 |
| 8/31 | 0320 | End material balance 12305; lineout 12306 |
| | 1120 | Start material balance 12306 |
| | 1920 | End material balance 12306; shutdown and cool reactor |
| 9/6 | | Pack reactor, pressure test, presulfide to 850°F |
| 9/10 | 0100 | Feed introduced |
| | 1700 | Start lineout 12307 |
| 9/11 | 0100 | Start material balance 12307 |
| | 0900 | End material balance 12307; lineout 12308 |
| | 1700 | Start material balance 12308 |

TABLE III-7 (CONT'D)

SERIES 123 RUN CHRONOLOGY

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|------------------|--|
| 9/12 | 0100 | End material balance 12308; lineout 12309 |
| | 0615 | Sudden 400 psig system pressure loss; no apparent reason, repressurized |
| | 0715 | System pressure increased to 2300 psig |
| | 0847 | Back pressure control valve replaced |
| | 0950 | Unit back on line |
| | 1200 | Unit pressure drops to 1850 psig; repressurized |
| | 1500 | Start material balance 12309 |
| | 1900 | System pressure loss 150 psig; repressurized |
| | 2315 | End material balance 12309; lineout 12310 |
| 9/13 | 0700 | Start material balance 12310 |
| | 0800 | Increase in reactor pressure; corrected |
| | 1000 | Gas line plugged |
| | 1200 | Gas line plugged |
| | 1300 | Gas line plugged |
| | 1500 | End material balance 12310; lineout 12311 |
| | 1830 | Gas line plugged |
| | 2100 | Start material balance 12311 |
| | 0500 | End material balance 12311; lineout 12312 |
| | 0800 | Pump failure |
| | 0900 | Pump failure |
| | 1000 | Pump failure |
| | 1200 | Start material balance 12312 |
| | 2000 | End material balance 12312, shutdown unit dump |

TABLE III-8

PARAMETER VARIATION HYDROTREATING

SERIES 111

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| OPERATING CONDITIONS | | | | | | | | | | | | |
| Temperature, °F | 604 | 598 | 597 | 647 | 648 | 648 | 700 | 699 | 703 | 751 | 752 | 754 |
| Pressure, PSIG | 521 | 521 | 509 | 522 | 513 | 523 | 511 | 515 | 517 | 519 | 500 | 486 |
| LHSV, Hr ⁻¹ | 1.01 | 1.90 | 2.90 | 3.94 | 1.74 | 0.92 | 0.88 | 1.97 | 3.81 | 2.89 | 1.60 | 0.80 |
| Hydrogen Rate, SCFB | 3948 | 4140 | 5486 | 4026 | 3734 | 4214 | 4600 | 4113 | 4283 | 5703 | 5315 | 5020 |
| MATERIAL BALANCE | | | | | | | | | | | | |
| Weight Percent of Feed | | | | | | | | | | | | |
| Feed | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Hydrogen In | 6.34 | 6.66 | 9.09 | 6.67 | 9.50 | 6.98 | 7.60 | 6.80 | 7.08 | 9.43 | 8.79 | 8.30 |
| Subtotal In | 106.54 | 106.66 | 109.09 | 106.67 | 109.50 | 106.98 | 107.60 | 106.80 | 107.08 | 109.43 | 108.79 | 108.30 |
| H ₂ O | (0.61) | (0.24) | (0.46) | (0.31) | (0.59) | (0.87) | (1.09) | (0.82) | (0.42) | (0.72) | (1.10) | (1.33) |
| H ₂ S | (0.37) | (0.32) | (0.30) | (0.32) | (0.37) | (0.43) | (0.49) | (0.48) | (0.35) | (0.49) | (0.54) | (0.55) |
| NH ₃ | (0.18) | - | - | (0.11) | (0.26) | (0.23) | (0.35) | (0.37) | (0.27) | (0.13) | (0.45) | (0.70) |
| Hydrogen Out | 6.22 | 6.39 | 8.21 | 5.71 | 9.10 | 6.16 | 7.75 | 6.71 | 7.16 | - | 9.02 | 8.53 |
| C ₁ | - | - | - | - | - | - | 0.08 | - | - | - | 0.21 | 0.42 |
| C ₂ | - | - | - | 0.05 | - | 0.22 | 0.77 | 0.04 | 0.01 | - | 0.04 | 1.57 |
| C ₃ | - | - | - | 0.02 | - | 0.23 | 0.95 | 0.05 | 0.02 | - | 0.06 | 2.39 |
| C ₄ | - | - | - | - | - | 0.24 | 1.37 | 0.04 | - | - | 0.05 | 2.75 |
| C ₅ | - | - | - | - | - | 0.23 | 1.91 | - | - | - | 0.07 | 2.43 |
| ISP - 400°F | 1.10 | 0.20 | 1.14 | 1.87 | 0.23 | 3.48 | 3.98 | 4.22 | 2.55 | 5.66 | 5.49 | 4.31 |
| 400 - 600°F | 21.83 | 21.26 | 21.66 | 22.29 | 25.14 | 26.21 | 26.82 | 25.11 | 16.09 | 30.01 | 28.29 | 32.15 |
| 600°F + | 73.69 | 81.29 | 67.43 | 75.25 | 71.90 | 68.60 | 74.31 | 62.80 | 79.94 | 69.30 | 60.09 | 43.71 |
| Subtotal Out | 104.00 | 109.70 | 98.9 | 105.93 | 107.59 | 106.94 | 119.87 | 100.64 | 106.81 | - | 105.41 | 100.84 |
| Total Liquids | 96.62 | 102.75 | 89.73 | 99.41 | 97.27 | 98.29 | 105.01 | 92.13 | 98.58 | - | 93.87 | 80.17 |
| Closure | 97.6 | 102.7 | 90.7 | 99.3 | 98.26 | 100.0 | 111.4 | 94.2 | 99.7 | - | 96.9 | 93.1 |
| Hydrogen Consumption, SCFB | 194 | 280 | 527 | 577 | 240 | 492 | - | - | - | - | - | - |

() - Calculated

TABLE III-9

PARAMETER VARIATION HYDROTREATING

SERIES 111

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| PRODUCT PROPERTIES (wt.%) | | | | | | | | | | | | |
| TOTAL LIQUID: | 26.0 | 25.5 | 24.6 | 25.4 | 25.6 | 26.2 | 28.6 | 27.1 | 26.2 | 27.7 | 28.9 | 30.7 |
| oAPI | 0.19 | 0.21 | 0.31 | 0.23 | 0.19 | 0.13 | 0.06 | 0.09 | 0.19 | 0.06 | 0.03 | 0.02 |
| ** Sulfur | (1.31) | (1.42) | (1.42) | (1.33) | (1.23) | (1.24) | (1.07) | (1.20) | (1.21) | (1.24) | (1.11) | (1.04) |
| ** Nitrogen | 0.93 | 0.96 | 1.01 | 0.95 | 0.91 | 1.07 | 0.82 | 0.93 | 0.93 | 0.90 | 0.84 | 0.70 |
| ** Basic Nitrogen | - | - | - | - | - | - | - | - | - | - | - | - |
| Oxygen | - | - | - | - | - | - | - | - | - | - | - | - |
| IBP-400°F | - | - | - | 43.3 | - | - | - | 43.7 | 45.7 | 42.9 | 44.3 | - |
| oAPI | 0.31 | * | 0.33 | 0.33 | 0.25 | 0.14 | 0.0049 | 0.07 | 0.21 | 0.12 | 0.04 | 0.02 |
| Sulfur | (1.13) | * | (1.41) | (1.40) | (1.25) | (1.30) | (0.93) | (1.26) | (1.71) | (1.58) | (1.27) | (0.82) |
| Nitrogen | 1.21 | * | 1.53 | 1.34 | 1.27 | 1.20 | 0.92 | 1.28 | 1.32 | 1.31 | 0.98 | 0.65 |
| Basic Nitrogen | 35.4 | 34.5 | 34.1 | 34.2 | 34.3 | 33.1 | 34.8 | 33.8 | 34.3 | 33.1 | 31.7 | 34.8 |
| 400-500°F | 0.14 | 0.14 | 0.31 | 0.26 | 0.16 | 0.13 | 0.03 | 0.04 | 0.14 | 0.06 | 0.02 | 0.01 |
| oAPI | (1.16) | (1.39) | (1.25) | (1.12) | (1.16) | (1.15) | (1.01) | (1.19) | (1.41) | (1.22) | (1.17) | (1.21) |
| Sulfur | 0.97 | 1.06 | 1.15 | 0.98 | 1.10 | 1.24 | 0.93 | 1.08 | 1.08 | 0.97 | 0.97 | 0.82 |
| Nitrogen | 22.6 | 22.2 | 21.3 | 23.3 | 22.5 | 22.5 | 25.0 | 24.5 | 23.5 | 24.3 | 25.3 | 25.9 |
| Basic Nitrogen | 0.21 | 0.22 | 0.31 | 0.22 | 0.20 | 0.24 | 0.08 | 0.11 | 0.20 | 0.05 | 0.04 | 0.02 |
| 600°F + | (1.36) | (1.61) | (1.54) | (1.41) | (1.26) | (1.27) | (1.10) | (1.21) | (1.15) | (1.23) | (1.07) | (0.94) |
| oAPI | 0.92 | 0.94 | 0.95 | 0.93 | 0.85 | 1.00 | 0.78 | 0.84 | 0.89 | 0.84 | 0.77 | 0.62 |
| Sulfur | | | | | | | | | | | | |
| Nitrogen | | | | | | | | | | | | |
| Basic Nitrogen | | | | | | | | | | | | |
| HETEROATOM REMOVAL (wt.%) | | | | | | | | | | | | |
| Desulfurization | 64.2 | 60.4 | 41.5 | 56.6 | 64.2 | 75.5 | 88.7 | 83.0 | 64.2 | 88.7 | 94.3 | 96.23 |
| Denitrogenation | 7.7 | -0- | -0- | 6.3 | 13.4 | 12.7 | 24.6 | 15.5 | 14.8 | 12.7 | 21.8 | 26.8 |
| Deoxygenation | - | - | - | - | - | - | - | - | - | - | - | - |

* - Insufficient Sample for Analysis

() - Calculated

** - Calculated from Fractionation Data

TABLE III-10

PARAMETER VARIATION HYDROTREATING

SERIES 112

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| OPERATING CONDITIONS | | | | | | | | | | | | |
| Temperature, °F | 603 | 600 | 603 | 631 | 633 | 632 | 696 | 697 | 699 | 753 | 753 | 756 |
| Pressure, PSIG | 1092 | 1081 | 1000 | 1000 | 998 | 1000 | 1000 | 1003 | 1004 | 1000 | 997 | 1000 |
| (HSV, Hr ⁻¹) | 0.92 | 1.41 | 2.46 | 2.50 | 1.80 | 0.92 | 0.83 | 1.76 | 3.32 | 3.63 | 1.85 | 1.01 |
| Hydrogen Rate, SCFB | 4318 | 3659 | 4591 | 4539 | 4504 | 4131 | 4920 | 4688 | 4519 | 4389 | 4473 | 4011 |
| MATERIAL BALANCE | | | | | | | | | | | | |
| Weight Percent of Feed | | | | | | | | | | | | |
| Feed | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Hydrogen In | 7.15 | 9.37 | 7.60 | 7.32 | 7.46 | 6.84 | 8.08 | 7.70 | 7.42 | 7.21 | 7.35 | 6.63 |
| Subtotal In | 107.15 | 109.37 | 107.60 | 107.52 | 107.46 | 106.84 | 102.08 | 107.70 | 107.42 | 107.21 | 107.35 | 106.63 |
| H ₂ O | (0.72) | (0.45) | (0.30) | (0.43) | (0.69) | (1.01) | - | (0.87) | (0.80) | (0.85) | (1.11) | (1.30) |
| H ₂ S | (0.40) | (0.23) | (0.29) | (0.35) | (0.45) | (0.44) | - | (0.50) | (0.48) | (0.54) | (0.55) | (0.51) |
| NH ₃ | (0.28) | (0.08) | (0.11) | (0.19) | (0.28) | (0.45) | - | (0.35) | (0.44) | (0.68) | (0.98) | (1.10) |
| Hydrogen Out | 6.42 | 8.94 | 6.96 | 6.42 | 6.81 | 6.33 | 4.89 | 5.66 | 6.10 | 5.49 | 5.40 | 3.30 |
| C ₁ | - | - | - | - | - | - | 0.17 | 0.09 | - | 0.16 | 0.42 | 0.55 |
| C ₂ | - | - | 0.02 | 0.98 | 0.44 | 0.24 | 0.70 | 0.80 | 0.02 | 0.24 | 0.69 | 1.40 |
| C ₃ | - | - | 0.02 | 0.94 | 0.49 | 0.24 | 0.72 | 0.67 | 0.03 | 0.26 | 0.76 | 1.52 |
| C ₄ | - | - | 0.04 | 0.43 | 0.46 | 0.23 | 0.67 | 0.37 | 0.02 | 0.24 | 0.71 | 1.33 |
| C ₅ | - | - | - | 0.92 | 0.52 | 0.26 | - | 0.11 | - | 0.20 | 0.58 | 1.05 |
| IBP-400°F | 1.54 | 1.68 | 1.66 | 0.45 | 0.88 | 2.61 | 0.84 | 4.46 | 4.42 | 4.54 | 8.13 | 7.00 |
| 400-600°F | 11.20 | 15.92 | 12.09 | 16.13 | 22.10 | 25.19 | 24.32 | 24.10 | 24.64 | 31.23 | 27.17 | 35.28 |
| 600°F + | 83.99 | 84.71 | 83.27 | 80.67 | 72.92 | 65.64 | 61.19 | 67.47 | 67.24 | 54.13 | 53.51 | 51.67 |
| Subtotal Out | 104.55 | 111.91 | 104.76 | 107.93 | 106.04 | 102.64 | 78.14 | 105.85 | 104.19 | 98.56 | 99.10 | 106.01 |
| Total Liquids | 96.73 | 102.31 | 97.02 | 97.25 | 95.90 | 93.44 | 66.35 | 96.03 | 96.30 | 89.90 | 88.71 | 93.95 |
| Closure | 97.6 | 102.3 | 97.4 | 100.4 | 98.7 | 96.1 | - | 98.3 | 97.0 | 91.9 | 93.1 | 99.4 |
| Hydrogen Consumption, SCFB | 439 | 319 | 391 | 662 | 391 | 306 | - | 1121 | 803 | 1048 | 1187 | 2015 |

() - Calculated

TABLE III-11

PARAMETER VARIATION HYDROTREATING

SERIES 112

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|----------------------------|----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| PRODUCT PROPERTIES (wt. %) | | | | | | | | | | | | |
| TOTAL LIQUID: | 27.1 | 26.1 | 25.1 | 26.2 | 26.6 | 27.7 | 31.0 | 28.7 | 27.3 | 30.0 | 31.4 | 34.2 |
| oAPI | 0.15 | 0.29 | 0.28 | 0.21 | 0.11 | 0.13 | 0.07 | 0.06 | 0.08 | 0.03 | 0.02 | 0.05 |
| **Sulfur | (1.23) | (1.32) | (1.37) | (1.30) | (1.24) | (1.12) | (0.82) | (1.01) | (1.10) | (0.96) | (0.69) | (0.55) |
| **Nitrogen | 0.94 | 0.96 | 1.06 | 0.93 | 0.90 | 0.91 | 0.57 | 0.72 | 0.90 | 0.69 | 0.53 | 0.43 |
| **Basic Nitrogen | - | - | - | - | - | - | 0.24 | 0.468 | 0.532 | - | 0.269 | - |
| Oxygen | - | - | - | - | - | - | - | 45.1 | 43.2 | 43.6 | 44.4 | - |
| IBP-400°F | - | - | - | - | - | - | - | - | - | - | - | - |
| oAPI | 0.03 | * | 0.48 | * | 0.05 | 0.06 | * | 0.03 | 0.04 | 0.02 | 0.02 | 0.07 |
| Sulfur | (1.12) | * | (1.62) | * | (1.34) | (1.05) | * | (0.79) | (1.37) | (1.05) | (0.71) | (0.33) |
| Nitrogen | 1.11 | * | 1.56 | * | 1.61 | 1.02 | * | 0.76 | 1.14 | 0.81 | 0.49 | 0.17 |
| Basic Nitrogen | 37.2 | 36.2 | 36.5 | 32.7 | 35.2 | 34.8 | 36.4 | 35.7 | 34.1 | 33.4 | 34.9 | 36.2 |
| 400-600°F | 0.05 | 0.26 | 0.54 | 0.14 | 0.05 | 0.02 | 0.07 | 0.02 | 0.01 | 0.02 | 0.04 | 0.05 |
| oAPI | (1.05) | (1.11) | (1.19) | (1.20) | (1.10) | (1.06) | (0.68) | (0.88) | (1.07) | (0.90) | (0.79) | (0.54) |
| Sulfur | 1.02 | 0.984 | 1.15 | 1.20 | 1.00 | 0.89 | 0.53 | 0.81 | 0.92 | 0.729 | 0.581 | 0.325 |
| Nitrogen | 25.0 | 23.3 | 23.4 | 21.8 | 22.8 | 23.8 | 24.6 | 24.8 | 23.5 | 24.5 | 26.3 | 27.8 |
| Basic Nitrogen | 0.16 | 0.30 | 0.26 | 0.22 | 0.13 | 0.18 | 0.07 | 0.08 | 0.11 | 0.03 | 0.01 | 0.05 |
| 600°F+ | (1.26) | (1.36) | (1.41) | (1.33) | (1.29) | (1.14) | (0.91) | (1.07) | (1.09) | (0.99) | (0.64) | (0.59) |
| oAPI | 0.93 | 0.95 | 1.04 | 0.88 | 0.86 | 0.92 | 0.59 | 0.69 | 0.88 | 0.86 | 0.51 | 0.55 |
| Sulfur | HETEROATOM REMOVAL (wt. %) | | | | | | | | | | | |
| Nitrogen | 71.7 | 45.3 | 47.2 | 60.4 | 79.2 | 75.5 | 86.8 | 88.7 | 84.9 | 94.3 | 96.2 | 90.6 |
| Basic Nitrogen | 13.4 | 7.0 | 3.9 | 8.5 | 12.7 | 21.1 | 42.3 | 78.9 | 22.5 | 32.4 | 57.4 | 61.3 |
| Desulfurization | - | - | - | - | - | - | 80.2 | 61.3 | 56.0 | - | 77.8 | - |

* INSUFFICIENT SAMPLE FOR ANALYSIS
 ** CALCULATED FROM FRACTIONATION DATA
 () CALCULATED

TABLE III-12

PARAMETER VARIATION HYDROTREATING

SERIES 113

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| OPERATING CONDITIONS | | | | | | | | | | | | |
| Temperature, °F | 603 | 601 | 602 | 650 | 651 | 650 | 700 | 704 | 701 | 762 | 756 | 754 |
| Pressure, PSIG | 2002 | 2007 | 2023 | 1997 | 1997 | 2014 | 2013 | 2003 | 2032 | 2006 | 1994 | 2017 |
| LHSV, Hr ⁻¹ | 1.00 | 1.60 | 3.48 | 3.75 | 1.69 | 0.95 | 0.92 | 2.13 | 3.95 | 4.14 | 1.88 | 1.15 |
| Hydrogen Rate, SCFB | 3813 | 5395 | 4964 | 4176 | 4968 | 4365 | 4451 | 3907 | 4466 | 3727 | 4263 | 3463 |
| MATERIAL BALANCE | | | | | | | | | | | | |
| Weight Percent of Feed | | | | | | | | | | | | |
| Feed | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Hydrogen In | 6.30 | 8.92 | 8.21 | 6.70 | 8.21 | 7.22 | 7.36 | 6.46 | 7.38 | 6.16 | 7.05 | 5.72 |
| Subtotal In | 106.30 | 108.92 | 108.21 | 106.70 | 108.21 | 107.22 | 107.36 | 106.46 | 107.38 | 106.16 | 107.05 | 105.72 |
| H ₂ O | (0.08) | (0.10) | (0.33) | (0.43) | (0.86) | (1.10) | (1.34) | (1.05) | (0.69) | (0.89) | (1.28) | (1.40) |
| H ₂ S | (0.37) | (0.34) | (0.23) | (0.33) | (0.44) | (0.37) | (0.53) | (0.45) | (0.44) | (0.41) | (0.44) | (0.52) |
| NH ₃ | (0.40) | (0.40) | (0.26) | (0.37) | (0.52) | (0.59) | (0.91) | (0.77) | (0.70) | (1.05) | (1.05) | (1.22) |
| Hydrogen Out | 4.82 | 6.68 | 5.69 | 5.15 | 6.07 | 5.19 | 5.81 | 4.89 | 4.57 | 4.33 | 4.36 | 3.25 |
| C ₁ | - | - | - | - | - | - | - | 0.07 | - | 0.18 | 0.31 | 0.26 |
| C ₂ | - | - | - | 0.29 | 0.11 | 0.08 | 0.27 | 0.95 | - | 0.71 | 0.86 | 0.96 |
| C ₃ | - | - | - | 0.25 | 0.11 | 0.08 | 0.58 | 0.97 | - | 0.77 | 2.66 | 1.03 |
| C ₄ | - | - | - | 0.48 | 0.09 | 0.05 | 1.11 | 0.97 | - | 0.82 | 2.04 | 1.03 |
| C ₅ | - | - | - | - | - | 0.02 | - | 0.72 | - | 0.40 | 0.79 | 0.41 |
| IBP - 400°F | 3.54 | 3.69 | 3.76 | - | 4.35 | - | 6.27 | 4.25 | 3.69 | - | 7.47 | 9.62 |
| 400 - 600°F | 29.47 | 29.21 | 28.07 | - | 27.52 | - | 31.67 | 30.71 | 31.17 | - | 35.58 | 37.40 |
| 600°F + | 66.94 | 63.67 | 66.51 | - | 63.73 | - | 57.25 | 58.02 | 60.39 | - | 49.15 | 46.73 |
| Subtotal Out | 105.62 | 104.09 | 104.85 | 105.85 | 103.79 | 107.25 | 103.74 | 103.82 | 101.65 | 106.79 | 106.78 | 103.86 |
| Total Liquids | 99.95 | 97.57 | 98.34 | 98.55 | 95.60 | 99.77 | 95.19 | 92.98 | 95.25 | 97.23 | 92.20 | 93.75 |
| Closure | 99.36 | 95.57 | 96.89 | 99.20 | 95.92 | 100.03 | 98.49 | 97.52 | 94.66 | 100.59 | 99.75 | 98.23 |
| Hydrogen Consumption, SCFB | 898 | 1355 | 1524 | 1064 | 1296 | 1224 | 935 | 952 | 1700 | 1109 | 1261 | 1498 |

() - Calculated

TABLE III-13

PARAMETER VARIATION HYDROTREATING

SERIES 113

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|----------------------------|---------|---------|---------|--------|---------|--------|---------|---------|---------|------|---------|---------|
| PRODUCT PROPERTIES (wt. %) | | | | | | | | | | | | |
| TOTAL LIQUID: | 27.3 | 26.5 | 25.7 | 26.9 | 27.8 | 38.7 | 31.6 | 29.9 | 28.2 | 31.4 | 33.7 | 34.7 |
| oAPI | 0.18 | 0.23 | 0.32 | 0.20 | 0.12 | 0.16 | 0.04 | 0.12 | 0.13 | 0.14 | 0.02 | 0.04 |
| ** Sulfur | (1.00) | (1.04) | (1.16) | (1.05) | (0.92) | (0.81) | (0.51) | (0.68) | (0.74) | 0.57 | (0.281) | (0.14) |
| ** Nitrogen | 0.78 | 0.93 | 0.92 | - | 0.82 | - | 0.32 | 0.57 | 0.72 | - | 0.22 | 0.08 |
| ** Basic Nitrogen | - | - | - | .919 | - | - | - | 0.402 | - | - | - | - |
| Oxygen | - | - | - | - | - | - | - | - | - | - | - | - |
| IBP-400°F | - | 44.5 | 43.3 | - | 44.9 | - | - | 45.9 | 46.4 | - | 46.2 | 46.7 |
| oAPI | 0.04 | 0.11 | 0.24 | - | 0.05 | - | 0.02 | 0.08 | 0.07 | - | 0.03 | 0.03 |
| Sulfur | (1.29) | (1.480) | (1.739) | * | (1.057) | * | (0.104) | (0.535) | (0.725) | * | (0.253) | (0.03) |
| Nitrogen | 1.406 | 1.613 | 1.666 | - | 1.062 | - | 0.102 | 0.428 | 0.787 | - | 0.111 | 0.025 |
| Basic Nitrogen | 34.3 | 33.7 | 33.3 | - | 34.8 | - | 36.9 | 36.0 | 35.0 | - | 36.8 | 37.3 |
| 400-600°F | 0.08 | 0.15 | 0.22 | - | 0.07 | - | 0.01 | 0.08 | 0.07 | - | 0.03 | 0.03 |
| oAPI | (0.91) | (0.959) | (1.159) | * | (0.964) | * | (0.29) | (0.693) | (0.779) | * | (0.27) | (0.10) |
| Sulfur | 0.628 | 0.991 | 0.965 | - | 0.890 | - | 0.238 | 0.564 | 0.721 | - | 0.199 | 0.066 |
| Nitrogen | 22.8 | 21.5 | 21.5 | - | 23.0 | - | 26.4 | 24.4 | 23.3 | - | 27.7 | 28.9 |
| Basic Nitrogen | 0.23 | 0.27 | 0.36 | - | 0.14 | - | 0.06 | 0.15 | 0.17 | - | 00.01 | 0.05 |
| 600°F + | (1.030) | (1.054) | (1.121) | * | (0.889) | * | (0.57) | - | - | * | (0.43) | (0.213) |
| oAPI | 0.810 | 0.858 | 0.864 | - | 0.777 | - | 0.383 | 0.590 | 0.720 | - | 0.260 | 0.102 |
| Sulfur | - | - | - | - | - | - | - | - | - | - | - | - |
| Nitrogen | - | - | - | - | - | - | - | - | - | - | - | - |
| Basic Nitrogen | - | - | - | - | - | - | - | - | - | - | - | - |
| HETEROATOM REMOVAL (wt. %) | | | | | | | | | | | | |
| Desulfurization | 66.0 | 56.6 | 39.6 | 62.3 | 77.4 | 69.8 | 92.5 | 77.4 | 75.5 | 73.6 | 96.2 | 92.5 |
| Denitrogenation | 28.6 | 25.6 | 17.1 | 25.0 | 34.3 | 42.1 | 63.6 | 51.4 | 47.1 | 61.0 | 80.0 | 90.0 |
| Deoxygenation | - | - | - | 23.4 | - | - | - | 66.5 | - | - | - | - |

* NO FRACTIONATION PERFORMED ON THESE PRODUCTS

** VALUES CALCULATED FROM FRACTIONATION DATA

() CALCULATED

TABLE III-14

PARAMETER VARIATION HYDROTREATING

SERIES 121

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| OPERATING CONDITIONS | | | | | | | | | | | | |
| Temperature, °F | 599 | 600 | 599 | 651 | 650 | 651 | 700 | 700 | 701 | 751 | 751 | 751 |
| Pressure, PSIG | 492 | 489 | 499 | 523 | 508 | 523 | 518 | 510 | 512 | 510 | 500 | 519 |
| LHSV, Hr ⁻¹ | 0.99 | 1.89 | 3.76 | 3.58 | 1.73 | 0.89 | 0.89 | 1.82 | 3.58 | 3.33 | 1.80 | 0.78 |
| Hydrogen Rate, SCFB | 4064 | 4144 | 4355 | 4403 | 4661 | 4512 | 4575 | 4413 | 4467 | 4553 | 4418 | 5333 |
| MATERIAL BALANCE | | | | | | | | | | | | |
| Weight Percent of Feed | | | | | | | | | | | | |
| Feed | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Hydrogen In | 6.71 | 6.85 | 7.19 | 7.27 | 7.70 | 7.45 | 6.89 | 7.29 | 7.38 | 7.52 | 7.30 | 9.84 |
| Subtotal In | 106.71 | 106.85 | 107.19 | 107.27 | 107.70 | 107.45 | 106.89 | 107.29 | 107.38 | 107.52 | 107.30 | 109.84 |
| H ₂ O | (0.58) | (0.40) | (0.25) | (0.61) | (0.62) | (1.05) | (1.18) | (0.82) | (0.50) | (0.72) | (1.02) | (1.31) |
| N ₂ | (0.14) | (0.06) | (0.09) | (0.29) | (0.34) | (0.46) | (0.52) | (0.49) | (0.43) | (0.44) | (0.53) | (0.50) |
| NH ₃ | (0.40) | (0.23) | (0.21) | (0.38) | (0.37) | (0.66) | (0.81) | (0.34) | (0.30) | (0.63) | (0.63) | (0.82) |
| Hydrogen Out | 5.62 | 5.72 | 5.91 | 5.85 | 6.33 | 5.81 | 4.67 | 5.54 | 5.19 | 5.37 | 5.42 | 7.00 |
| C ₁ | - | - | - | - | - | - | 0.10 | - | - | 0.12 | 0.31 | 0.27 |
| C ₂ | - | - | - | - | - | - | 0.30 | 0.24 | 0.34 | 0.55 | 0.70 | 1.14 |
| C ₃ | - | - | - | - | - | - | 0.78 | 0.26 | 0.12 | 0.55 | 0.63 | 1.17 |
| C ₄ | - | - | - | - | - | - | 2.05 | 0.91 | 0.35 | 0.38 | 0.43 | 0.88 |
| C ₅ | - | - | - | - | - | - | 1.67 | 0.23 | 0.28 | 0.08 | 0.41 | 0.60 |
| IBP-400°F | 2.70 | 6.64 | 3.52 | 1.13 | 2.29 | 2.19 | 4.41 | 4.55 | 4.17 | 3.27 | 4.06 | 3.62 |
| 400-600°F | 19.15 | 8.93 | 24.66 | 26.51 | 28.48 | 26.39 | 25.75 | 24.18 | 29.55 | 30.72 | 29.01 | 39.03 |
| 600°F + | 78.32 | 83.99 | 70.10 | 64.92 | 64.16 | 58.69 | 56.75 | 68.72 | 64.48 | 62.05 | 64.16 | 51.02 |
| Subtotal Out | 106.91 | 103.97 | 104.74 | 99.69 | 102.66 | 95.25 | 99.00 | 106.28 | 105.71 | 104.88 | 107.31 | 107.36 |
| Total Liquids | 100.17 | 99.56 | 98.28 | 92.56 | 94.93 | 87.27 | 86.91 | 97.45 | 99.20 | 96.04 | 97.23 | 93.67 |
| Closure | 100.2 | 99.2 | 97.7 | 92.9 | 95.3 | 88.6 | 92.6 | 99.1 | 98.4 | 97.5 | 100.0 | 97.7 |
| Hydrogen Consumption, SCFB | 659 | 686 | 778 | 864 | 829 | 992 | 1473 | 1058 | 1325 | 1303 | 1137 | 1720 |

() Calculated from inlet and outlet liquid properties

TABLE III-15

PARAMETER VARIATION HYDROTREATING

SERIES 121

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---------------------------|---------------------------|--------|--------|---------|--------|--------|--------|---------|--------|--------|--------|---------|
| PRODUCT PROPERTIES (wt.%) | | | | | | | | | | | | |
| TOTAL LIQUID: | 25.3 | 27.0 | - | 25.3 | 26.0 | 26.3 | 28.4 | 27.5 | 25.8 | 27.5 | 28.6 | 30.8 |
| oAPI | 0.38 | 0.47 | 0.46 | 0.30 | 0.23 | 0.13 | 0.03 | 0.07 | 0.13 | 0.12 | 0.03 | 0.07 |
| Sulfur | (1.07) | (1.22) | (1.23) | (1.17) | (1.15) | (0.99) | (0.87) | (1.08) | (1.16) | (0.92) | (0.91) | (0.77) |
| Nitrogen | 0.85 | 1.03 | 0.90 | 1.01 | 1.02 | 0.95 | 0.67 | 0.82 | 0.89 | 0.81 | 0.78 | 0.62 |
| Basic Nitrogen | - | - | - | (0.767) | - | - | - | (0.501) | - | - | - | - |
| Oxygen | - | 39.9 | 41.9 | - | - | - | 45.0 | 43.4 | 41.9 | 43.6 | 45.7 | - |
| IBP-400°F | - | 0.49 | 0.51 | 0.45 | 0.34 | 0.25 | 0.01 | 0.06 | 0.20 | 0.18 | 0.04 | 0.07 |
| oAPI | (1.50) | (1.53) | (1.73) | (1.72) | (1.61) | (1.78) | (0.89) | (1.32) | (1.62) | (1.39) | (1.13) | (0.70) |
| Sulfur | 1.265 | 1.262 | 1.442 | 1.430 | 1.54 | 1.48 | 0.708 | 1.506 | 1.313 | 1.083 | 0.930 | 0.631 |
| Nitrogen | 33.4 | 33.7 | 32.2 | 33.6 | 33.0 | 33.2 | 34.6 | 33.9 | 32.8 | 33.4 | 34.0 | 34.3 |
| Basic Nitrogen | 0.39 | 0.38 | 0.48 | 0.30 | 0.22 | 0.13 | 0.02 | 0.06 | 0.10 | 0.13 | 0.03 | 0.06 |
| oAPI | (1.08) | (1.10) | (1.12) | (1.07) | (1.46) | (1.47) | (0.85) | (0.98) | (1.02) | (0.97) | (1.05) | (1.02) |
| Sulfur | 0.983 | 0.995 | 0.907 | 0.875 | 1.04 | 1.05 | 0.701 | 0.924 | 0.902 | 0.991 | 0.883 | 0.727 |
| Nitrogen | 23.0 | 23.0 | 21.8 | 21.5 | 21.4 | 22.2 | 24.2 | 23.7 | 22.0 | 24.0 | 25.0 | 25.8 |
| Basic Nitrogen | 0.37 | 0.46 | 0.45 | 0.30 | 0.23 | 0.13 | 0.03 | 0.07 | 0.14 | 0.11 | 0.03 | 0.08 |
| oAPI | (1.05) | (1.17) | (1.28) | (1.27) | (1.25) | (1.23) | (0.95) | (1.10) | (1.21) | (1.13) | (1.02) | (1.121) |
| Sulfur | 0.780 | 0.886 | 0.873 | 0.978 | 0.959 | 0.965 | 0.645 | 0.781 | 0.826 | 0.785 | 0.720 | 0.501 |
| Nitrogen | HETEROATOM REMOVAL (wt.%) | | | | | | | | | | | |
| Basic Nitrogen | 38.3 | 11.3 | 13.2 | 43.4 | 56.6 | 75.5 | 94.3 | 86.8 | 75.5 | 77.4 | 94.3 | 86.8 |
| Desulfurization | 23.6 | 12.9 | 10.7 | 15.4 | 17.9 | 28.3 | 37.9 | 22.0 | 17.1 | 34.3 | 35.0 | 45.0 |
| Denitrogenation | - | - | - | 36.6 | - | - | - | 58.6 | - | - | - | - |
| Deoxygenation | - | - | - | - | - | - | - | - | - | - | - | - |

() - Calculated

TABLE III-16

PARAMETER VARIATION HYDROTREATING

SERIES 122

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| OPERATING CONDITIONS | | | | | | | | | | | | |
| Temperature, °F | 602 | 604 | 605 | 652 | 654 | 635 | 703 | 704 | 704 | 756 | 758 | 752 |
| Pressure, PSIG | 1021 | 1003 | 1000 | 1000 | 1024 | 1018 | 998 | 1000 | 996 | 995 | 998 | 999 |
| LHSV, Hr ⁻¹ | 0.81 | 1.84 | 3.53 | 3.52 | 1.89 | 0.826 | 0.898 | 1.89 | 3.53 | 3.68 | 1.62 | 0.66 |
| Hydrogen Rate, SCFB | 4937 | 4375 | 3948 | 4536 | 4264 | 4850 | 4476 | 4258 | 5012 | 4378 | 4971 | 6051 |
| MATERIAL BALANCE | | | | | | | | | | | | |
| Weight Percent of Feed | | | | | | | | | | | | |
| Feed | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Hydrogen In | 8.15 | 7.23 | 6.52 | 7.49 | 7.04 | 8.01 | 7.39 | 7.04 | 8.28 | 7.24 | 8.22 | 10.00 |
| Subtotal In | 108.15 | 107.23 | 106.52 | 107.49 | 107.04 | 108.01 | 107.39 | 107.04 | 108.28 | 107.24 | 108.22 | 110.00 |
| H ₂ O | (0.88) | (0.46) | (0.33) | (0.44) | (0.83) | (0.04) | (0.95) | (0.99) | (0.83) | (0.86) | (1.13) | (1.34) |
| H ₂ S | (0.39) | (0.29) | (0.23) | (0.39) | (0.49) | (0.20) | (0.34) | (0.34) | (0.48) | (0.51) | (0.54) | (0.53) |
| NH ₃ | (0.44) | (0.36) | (0.27) | (0.28) | (0.60) | (0.23) | (0.98) | (0.69) | (0.40) | (0.90) | (0.98) | (1.41) |
| Hydrogen Out | 7.22 | 5.43 | 5.97 | 6.21 | 5.88 | 6.06 | 5.33 | 5.60 | 5.76 | 5.70 | 6.14 | 7.34 |
| C ₁ | - | - | - | - | - | - | 0.12 | 0.21 | 0.30 | 0.11 | 0.22 | - |
| C ₂ | 0.01 | - | - | - | - | 0.11 | 1.45 | 0.26 | 0.29 | 0.56 | 1.04 | 2.09 |
| C ₃ | 0.01 | - | - | - | - | 0.08 | 2.08 | 0.27 | 0.28 | 0.57 | 1.01 | 2.63 |
| C ₄ | - | - | - | - | - | - | 2.78 | 0.30 | 0.28 | 0.67 | 0.93 | 3.88 |
| C ₅ | - | - | - | - | - | - | 2.13 | 0.33 | 0.28 | 0.31 | 0.72 | 0.69 |
| IBP-400°F | 4.67 | 3.52 | 3.30 | 1.20 | 3.88 | 4.03 | 4.69 | 5.03 | 3.26 | 4.24 | 2.98 | 9.97 |
| 400-600°F | 27.42 | 29.11 | 17.16 | 25.14 | 25.88 | 42.50 | 33.08 | 31.96 | 28.53 | 33.72 | 36.71 | 40.43 |
| 600°F + | 63.71 | 67.84 | 74.22 | 72.51 | 66.59 | 91.36 | 54.27 | 59.40 | 65.52 | 52.09 | 54.17 | 52.28 |
| Subtotal Out | 104.75 | 107.01 | 101.46 | 106.17 | 104.15 | 144.61 | 108.40 | 105.57 | 107.21 | 100.24 | 106.57 | 129.59 |
| Total Liquids | 95.80 | 100.47 | 94.68 | 98.85 | 96.35 | 137.89 | 92.04 | 96.39 | 97.31 | 90.05 | 93.86 | 109.68 |
| Closure | 96.9 | 99.8 | 95.2 | 98.8 | 97.3 | 134.7 | 100.9 | 98.6 | 99.0 | 93.5 | 99.17 | 117.8 |
| Hydrogen Consumption, SCFB | 564 | 1088 | 346 | 778 | 705 | 1178 | 1251 | 868 | 920 | 927 | 1257 | 1608 |

() - Calculated

TABLE III-17

PARAMETER VARIATION HYDROTREATING

SERIES 122

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|----------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|--------|
| PRODUCT PROPERTIES (wt. %) | | | | | | | | | | | | |
| TOTAL LIQUID: | 27.5 | 26.0 | 25.3 | 26.2 | 27.1 | 28.9 | 31.1 | 29.2 | 26.8 | 29.6 | 31.5 | 33.7 |
| API | (0.17) | 0.25 | 0.33 | 0.17 | 0.07 | 0.09 | 0.03 | 0.04 | 0.08 | 0.06 | 0.02 | 0.01 |
| ** Sulfur | (1.08) | (1.10) | (1.24) | (1.18) | (0.94) | (0.88) | (0.84) | (0.86) | (1.10) | (0.73) | (0.63) | (0.22) |
| ** Nitrogen | (0.809) | 0.86 | 0.939 | 0.93 | 0.855 | 0.66 | 0.37 | 0.59 | 0.73 | 0.65 | 0.41 | 0.135 |
| ** Basic Nitrogen | - | - | - | - | 0.497 | 0.587 | 0.401 | 0.339 | 0.489 | - | 0.227 | - |
| Oxygen | - | - | - | - | - | - | - | - | - | - | - | - |
| IBP-400°F | - | - | 42.0 | - | - | - | - | - | 44.4 | 46.3 | - | 46.1 |
| API | 0.07 | 0.15 | 0.33 | 0.14 | 0.032 | - | 0.03 | 0.01 | 0.03 | 0.07 | 0.002 | 0.01 |
| Sulfur | (1.179) | (1.686) | (1.774) | (1.309) | (1.190) | - | (0.367) | (0.683) | (2.193) | (0.823) | (0.484) | (0.12) |
| Nitrogen | 1.084 | 1.493 | 1.406 | 1.13 | 1.05 | - | 0.184 | 0.462 | 0.944 | 0.555 | 0.321 | 0.117 |
| Basic Nitrogen | 33.9 | 33.8 | 33.6 | 38.2 | 34.6 | 35.5 | 36.4 | 35.4 | 34.5 | 34.5 | 36.0 | 36.2 |
| 400-600°F | 0.08 | 0.18 | 0.26 | 0.11 | 0.035 | 0.04 | 0.04 | 0.01 | 0.01 | 0.03 | 0.04 | 0.01 |
| API | (1.142) | (0.928) | (1.093) | (1.258) | - | (0.775) | (0.545) | (0.810) | (1.158) | (0.957) | (0.624) | (0.17) |
| Sulfur | 0.832 | 0.873 | 0.954 | 1.04 | - | 0.651 | 0.337 | 0.598 | 0.722 | 0.721 | 0.452 | 0.152 |
| Nitrogen | 22.6 | 21.6 | 21.9 | 24.5 | 23.5 | 25.6 | 25.2 | - | 23.6 | 23.8 | 26.3 | 27.8 |
| Basic Nitrogen | 0.22 | 0.28 | 0.34 | 0.19 | 0.082 | 0.11 | 0.02 | 0.05 | 0.11 | 0.08 | 0.01 | 0.02 |
| 600°F + | (1.042) | (1.146) | (1.252) | (1.144) | (1.158) | (0.962) | (0.722) | (0.897) | (1.070) | (0.919) | (0.659) | (0.25) |
| API | 0.779 | 0.831 | 0.882 | 0.888 | 0.854 | 0.889 | 0.413 | 0.596 | 0.717 | 0.604 | 0.380 | 0.126 |
| Sulfur | - | - | - | - | - | - | - | - | - | - | - | - |
| Nitrogen | - | - | - | - | - | - | - | - | - | - | - | - |
| Basic Nitrogen | - | - | - | - | - | - | - | - | - | - | - | - |
| HETEROATOM REMOVAL (wt. %) | | | | | | | | | | | | |
| Desulfurization | 67.9 | 52.8 | 37.7 | 67.9 | 86.8 | 83.0 | 94.3 | 94.3 | 84.9 | 88.7 | 96.2 | 96.2 |
| Denitrogenation | 22.9 | 24.4 | 11.4 | 45.7 | 32.9 | 37.1 | 54.3 | 38.6 | 24.4 | 47.9 | 55.0 | 84.3 |
| Deoxygenation | - | - | - | - | 58.93 | 51.49 | 66.86 | 70.33 | 59.59 | - | 81.24 | - |

() - Calculated

** - Calculated from Fractionation Data

TABLE III-18

PARAMETER VARIATION HYDROTREATING

SERIES 123

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Temperature, °F | 606 | 603 | 604 | 635 | 628 | 654 | 704 | 707 | 718 | 765 | 753 | 751 |
| Pressure, PSIG | 2012 | 1993 | 2009 | 2003 | 2017 | 2009 | 2009 | 2030 | 1996 | 2062 | 2008 | 1997 |
| LHSV, Hr ⁻¹ | 0.93 | 1.87 | 3.67 | 3.61 | 1.60 | 0.90 | 1.16 | 1.68 | 3.58 | 3.85 | 1.71 | 0.84 |
| Hydrogen Rate, SCFB | 4369 | 4971 | 4508 | 4613 | 3661 | 4502 | 3791 | 4833 | 4664 | 4626 | 4850 | 4901 |
| OPERATING CONDITIONS | | | | | | | | | | | | |
| MATERIAL BALANCE | | | | | | | | | | | | |
| Weight Percent of Feed | | | | | | | | | | | | |
| Feed | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Hydrogen In | 7.21 | 8.21 | 7.45 | 7.62 | 9.35 | 7.43 | 6.25 | 7.97 | 7.69 | 7.63 | 8.00 | 8.08 |
| Subtotal In | 107.21 | 108.21 | 107.45 | 107.62 | 109.35 | 107.43 | 106.25 | 107.97 | 107.69 | 107.63 | 108.00 | 108.08 |
| H ₂ O | (0.98) | (0.61) | (0.02) | (0.57) | (0.95) | (2.19) | (1.30) | (1.29) | (1.09) | (0.97) | (1.27) | (1.43) |
| H ₂ S | (0.42) | (0.36) | (0.15) | (0.36) | (0.43) | (0.44) | (0.51) | (0.50) | (0.52) | (0.50) | (0.49) | (0.52) |
| NH ₃ | (0.34) | (0.16) | (0.00) | (0.25) | (0.67) | (0.81) | (1.35) | (1.30) | (1.16) | (1.28) | (1.46) | (1.65) |
| Hydrogen Out | 5.27 | 6.23 | 6.67 | 5.23 | 7.79 | 5.76 | 3.40 | 6.05 | - | 4.74 | 4.40 | 4.75 |
| C ₁ | - | - | - | - | - | - | - | 0.06 | - | 0.12 | 0.01 | 0.36 |
| C ₂ | 0.08 | 0.26 | 0.04 | 0.20 | 0.55 | 0.16 | 1.24 | 1.83 | 1.71 | 0.92 | 2.16 | 0.43 |
| C ₃ | 0.12 | 0.14 | - | 0.13 | 0.44 | 0.12 | 1.00 | 1.31 | 1.28 | 0.71 | 0.45 | 0.21 |
| C ₄ | - | 0.15 | - | 1.19 | - | - | 0.19 | 0.69 | 5.52 | 0.40 | 0.27 | 0.14 |
| C ₅ | - | 0.13 | - | - | 0.37 | - | 0.17 | 0.25 | 0.15 | 0.19 | 0.20 | 0.05 |
| ISP - 400°F | 3.07 | 2.68 | 4.17 | 1.94 | 2.15 | 6.01 | 1.23 | 8.45 | 3.86 | 8.52 | 17.67 | 8.57 |
| 400 - 600°F | 32.11 | 32.95 | 37.14 | 34.41 | 34.88 | 36.61 | 36.04 | 36.02 | 25.90 | 35.88 | 40.87 | 39.38 |
| 600°F + | 63.2 | 63.35 | 72.80 | 60.58 | 61.28 | 59.67 | 57.80 | 55.84 | 43.54 | 52.13 | 42.04 | 50.57 |
| Subtotal Out | 103.62 | 107.04 | 120.98 | 104.86 | 109.51 | 110.77 | 104.25 | 113.59 | 90.45 | 106.36 | 111.29 | 108.06 |
| Total Liquids | 98.40 | 98.98 | 116.11 | 96.93 | 98.31 | 102.29 | 95.07 | 100.31 | 73.30 | 96.53 | 100.58 | 98.52 |
| Closure | 98.5 | 98.9 | 112.16 | 97.4 | 100.1 | 103.1 | 98.1 | 105.2 | 84.0 | 98.8 | 103.0 | 100.0 |
| Hydrogen Consumption, SCFB | 1053 | 1189 | 514 | 144 | 848 | 1006 | 1775 | 1162 | 1189 | 1750 | 2180 | 2023 |

() - Calculated

TABLE III-19

PARAMETER VARIATION HYDROTREATING

SERIES 123

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|---------|
| PRODUCT PROPERTIES (wt. %) | | | | | | | | | | | | |
| TOTAL LIQUID: | | | | | | | | | | | | |
| oAPI | 27.3 | 26.1 | 25.7 | 26.5 | 28.2 | 28.6 | 31.2 | 31.6 | 29.6 | 31.8 | 33.0 | 34.7 |
| Sulfur | 0.14 | 0.19 | 0.30 | 0.20 | 0.13 | 0.11 | 0.06 | 0.06 | 0.08 | 0.06 | 0.07 | 0.04 |
| Nitrogen | (1.14) | (1.28) | (1.33) | (1.23) | (0.86) | (0.72) | (0.30) | (0.33) | (0.61) | (0.36) | (0.20) | (0.044) |
| Basic Nitrogen | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Oxygen | --- | --- | --- | --- | --- | --- | --- | 0.14 | --- | --- | --- | --- |
| IBP-400°F | * | * | * | * | * | * | * | * | * | * | * | * |
| oAPI | | | | | | | | | | | | |
| Sulfur | | | | | | | | | | | | |
| Nitrogen | | | | | | | | | | | | |
| Basic Nitrogen | | | | | | | | | | | | |
| 400-600°F | | | | | | | | | | | | |
| oAPI | | | | | | | | | | | | |
| Sulfur | | | | | | | | | | | | |
| Nitrogen | | | | | | | | | | | | |
| Basic Nitrogen | | | | | | | | | | | | |
| 600°F + | | | | | | | | | | | | |
| oAPI | | | | | | | | | | | | |
| Sulfur | | | | | | | | | | | | |
| Nitrogen | | | | | | | | | | | | |
| Basic Nitrogen | | | | | | | | | | | | |
| HETEROATOM REMOVAL (wt. %) | | | | | | | | | | | | |
| Desulfurization | 73.6 | 64.2 | 43.4 | 62.3 | 75.5 | 79.2 | 88.7 | 88.7 | 84.9 | 88.7 | 86.8 | 92.5 |
| Denitrogenation | 18.6 | 8.6 | 5.0 | 12.1 | 38.6 | 48.6 | 78.6 | 76.4 | 56.4 | 74.3 | 65.7 | 96.9 |
| Deoxygenation | | | | | | | | 89.2 | | | | |

* SIMULATED DISTILLATION PERFORMED ONLY

TABLE III-20

PARAMETER VARIATION HYDROTREATING SERIES 111

| HYDROGEN DISTRIBUTION | | | | | | | | | | | | |
|--------------------------------|-----|-----|-----|-----|-----|-----|---|---|---|----|----|----|
| Percent of Total | | | | | | | | | | | | |
| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| H ₂ S | 7 | 4 | 2 | 2 | 5 | 3 | - | - | - | - | - | - |
| NH ₃ | 3 | 0 | 0 | 2 | 12 | 5 | - | - | - | - | - | - |
| H ₂ O | 21 | 6 | 6 | 4 | 16 | 12 | - | - | - | - | - | - |
| C ₁ -C ₅ | 0 | 0 | 0 | 1 | 0 | 21 | - | - | - | - | - | - |
| Liquid | 69 | 90 | 92 | 91 | 67 | 59 | - | - | - | - | - | - |
| Total, SCFB | 194 | 280 | 527 | 577 | 240 | 492 | - | - | - | - | - | - |

TABLE III-21

PARAMETER VARIATION HYDROTREATING SERIES 112

| HYDROGEN DISTRIBUTION | | | | | | | | | | | | |
|--------------------------------|-----|-----|-----|-----|-----|-----|---|------|-----|------|------|------|
| Percent of Total | | | | | | | | | | | | |
| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| H ₂ S | 3 | 3 | 3 | 2 | 4 | 5 | - | 2 | 2 | 2 | 2 | 1 |
| NH ₃ | 7 | 3 | 3 | 3 | 8 | 16 | - | 5 | 6 | 7 | 9 | 6 |
| H ₂ O | 11 | 9 | 5 | 5 | 12 | 22 | - | 5 | 7 | 5 | 6 | 4 |
| C ₁ -C ₅ | 0 | 0 | 2 | 54 | 53 | 34 | - | 21 | 1 | 12 | 31 | 33 |
| Liquid | 79 | 85 | 87 | 36 | 23 | 23 | - | 67 | 84 | 74 | 52 | 56 |
| Total, SCFB | 439 | 319 | 391 | 662 | 391 | 306 | - | 1121 | 803 | 1048 | 1187 | 2015 |

TABLE III-22

PARAMETER VARIATION HYDROTREATING

SERIES 113

| HYDROGEN DISTRIBUTION | | | | | | | | | | | | |
|--------------------------------|-----|------|------|------|------|------|-----|-----|------|------|------|------|
| Percent of Total | | | | | | | | | | | | |
| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| H ₂ S | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 1 | 1 | 2 | 1 |
| NH ₃ | 5 | 3 | 2 | 4 | 4 | 5 | 10 | 9 | 4 | 10 | 10 | 9 |
| H ₂ O | 1 | 1 | 1 | 3 | 4 | 6 | 10 | 7 | 3 | 5 | 7 | 6 |
| C ₁ -C ₅ | 0 | 0 | 0 | 12 | 3 | 2 | 23 | 43 | 0 | 29 | 58 | 28 |
| Liquid | 93 | 95 | 96 | 80 | 88 | 86 | 55 | 39 | 92 | 55 | 23 | 56 |
| Total, SCFB | 898 | 1355 | 1524 | 1064 | 1296 | 1224 | 935 | 952 | 1700 | 1109 | 1261 | 1498 |

TABLE III-23

PARAMETER VARIATION HYDROTREATING

SERIES 121

| HYDROGEN DISTRIBUTION | | | | | | | | | | | | |
|--------------------------------|-----|-----|-----|-----|-----|-----|------|------|------|------|------|------|
| Percent of Total | | | | | | | | | | | | |
| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| H ₂ S | 1 | 0 | 0 | 1 | 1 | 2 | 1 | 2 | 1 | 1 | 2 | 1 |
| NH ₃ | 6 | 4 | 3 | 5 | 5 | 7 | 6 | 3 | 2 | 5 | 6 | 5 |
| H ₂ O | 6 | 4 | 2 | 5 | 6 | 7 | 6 | 5 | 3 | 4 | 6 | 5 |
| C ₁ -C ₅ | 0 | 0 | 0 | 0 | 0 | 0 | 39 | 17 | 9 | 15 | 25 | 27 |
| Liquid | 87 | 92 | 95 | 89 | 88 | 84 | 48 | 73 | 85 | 75 | 61 | 62 |
| Total, SCFB | 659 | 686 | 778 | 864 | 829 | 992 | 1473 | 1058 | 1325 | 1303 | 1137 | 1720 |

TABLE III-24

PARAMETER VARIATION HYDROTREATING SERIES 122

| HYDROGEN DISTRIBUTION | | | | | | | | | | | | |
|--------------------------------|-----|------|-----|-----|-----|------|------|-----|-----|-----|------|------|
| Percent of Total | | | | | | | | | | | | |
| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| H ₂ S | 2 | 1 | 2 | 2 | 2 | 1 | 2 | 2 | 2 | 2 | 2 | 1 |
| NH ₃ | 8 | 4 | 8 | 4 | 9 | 2 | 8 | 8 | 5 | 10 | 8 | 9 |
| H ₂ O | 11 | 3 | 6 | 4 | 8 | 0 | 5 | 8 | 6 | 6 | 6 | 6 |
| C ₁ -C ₅ | 0 | 0 | 0 | 0 | 0 | 2 | 74 | 18 | 18 | 27 | 35 | 63 |
| Liquid | 79 | 92 | 84 | 90 | 81 | 95 | 11 | 64 | 69 | 55 | 49 | 21 |
| Total, SCFB | 564 | 1088 | 346 | 778 | 705 | 1178 | 1251 | 868 | 920 | 927 | 1257 | 1608 |

TABLE III-25

PARAMETER VARIATION HYDROTREATING

SERIES 123

| HYDROGEN DISTRIBUTION | | | | | | | | | | | | |
|--------------------------------|------|------|-----|------|-----|------|------|------|------|------|------|------|
| Percent of Total | | | | | | | | | | | | |
| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| H ₂ S | 1 | 1 | 1 | 1 | 2 | 2 | 1 | 2 | 2 | 1 | 1 | 1 |
| NH ₃ | 3 | 1 | 0 | 2 | 8 | 9 | 8 | 12 | 10 | 8 | 7 | 9 |
| H ₂ O | 6 | 3 | 0 | 3 | 7 | 8 | 5 | 7 | 6 | 4 | 4 | 5 |
| C ₁ -C ₅ | 2 | 6 | 1 | 11 | 16 | 3 | 17 | 41 | 79 | 15 | 17 | 7 |
| Liquid | 88 | 89 | 98 | 83 | 67 | 78 | 69 | 38 | 3 | 72 | 71 | 78 |
| Total, SCFB | 1053 | 1189 | 514 | 1445 | 848 | 1008 | 1725 | 1162 | 1189 | 1750 | 2180 | 2023 |

DISCUSSION

Note that some product values have been estimated or calculated, as indicated by ().

The reader should note that the quoted full-range data are for unstabilized product and may not accurately portray product properties. The fractionation data are designed to provide better quantification of this information.

All synthetic materials are extremely sensitive to product work-up procedures. A particular case in point is the nitrogen and sulfur contents of the fractionated naphtha (IBP-400) products. These data are very high, and result from sulfur and nitrogen washing of the fractionator overhead glassware. During the early stages of the fractionations, sulfur and/or ammonia deposition is visible on the product collection system. As system temperature increases, condensing liquid effectively washes this material into the first collected liquid fractions. This could be corrected by separate stripping operations or other means, but has not been accomplished to date due to extra manpower requirements.

Results from runs 111 and 121 are somewhat erratic, as might be expected for shale oil processing at this low temperature/hydrogen availability. This is due to the fact that at these operating severities, significant quantities of ammonia and sulfur compounds were produced. These materials caused significant pressure regulator problems due to deposition on the stem and seat. Water injection prior to

the high-pressure flash should have been practiced, and will be in the future.

Figures III-2 through III-5 present the desulfurization and denitrogenation response obtained for these materials. Correlations between denitrogenation and desulfurization are presented in Figures III-6 and III-7. An interesting aspect of these figures is the apparent pressure functionality of this relationship for the cobalt molybdate catalyst, whereas the nickel molybdate does not show this apparent response. The second order denitrogenation response to space velocity is shown in Figure III-8.

Finally, hydrogen consumption versus product nitrogen is shown in Figure III-9.

2. M-SERIES STUDIES

SUMMARY

Crude in situ shale oil was processed for a nominal 100 hours at constant (target) operating conditions in order to evaluate initial catalyst stability, as well as determine the length of time required to reach full catalyst equilibration. Studies were made over both cobalt molybdate and nickel molybdate hydrotreating catalysts. Both catalysts produced denitrogenation ranging 20-30 percent and desulfurization of 60-70 percent, with the nickel molybdate catalyst showing slightly higher heteroatom

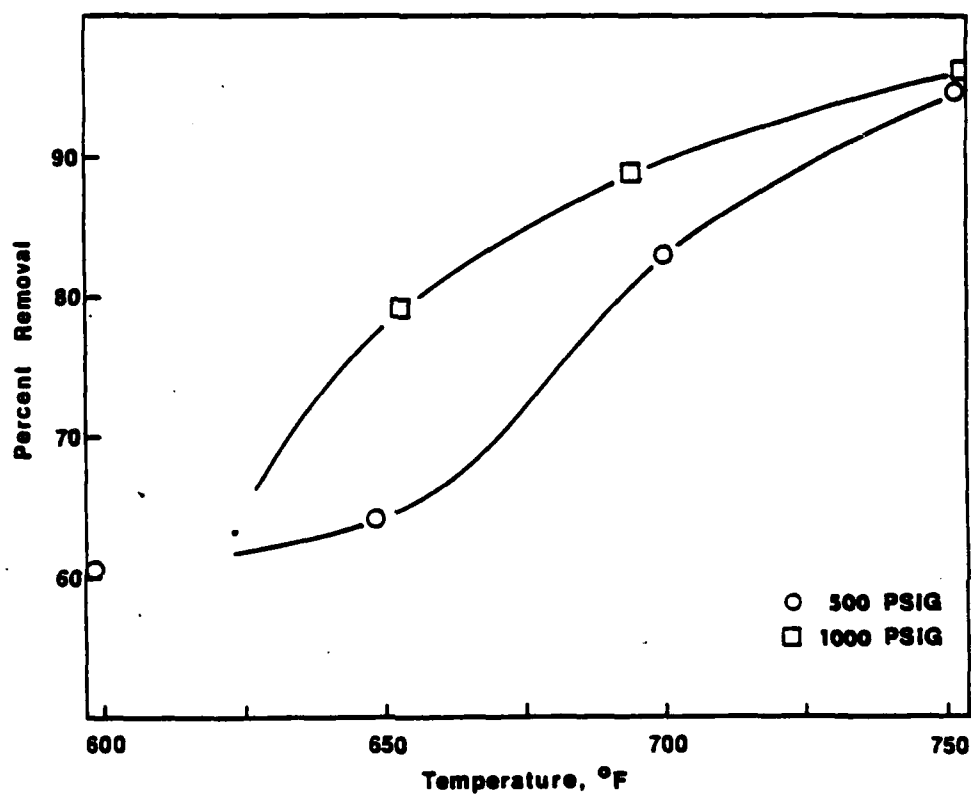
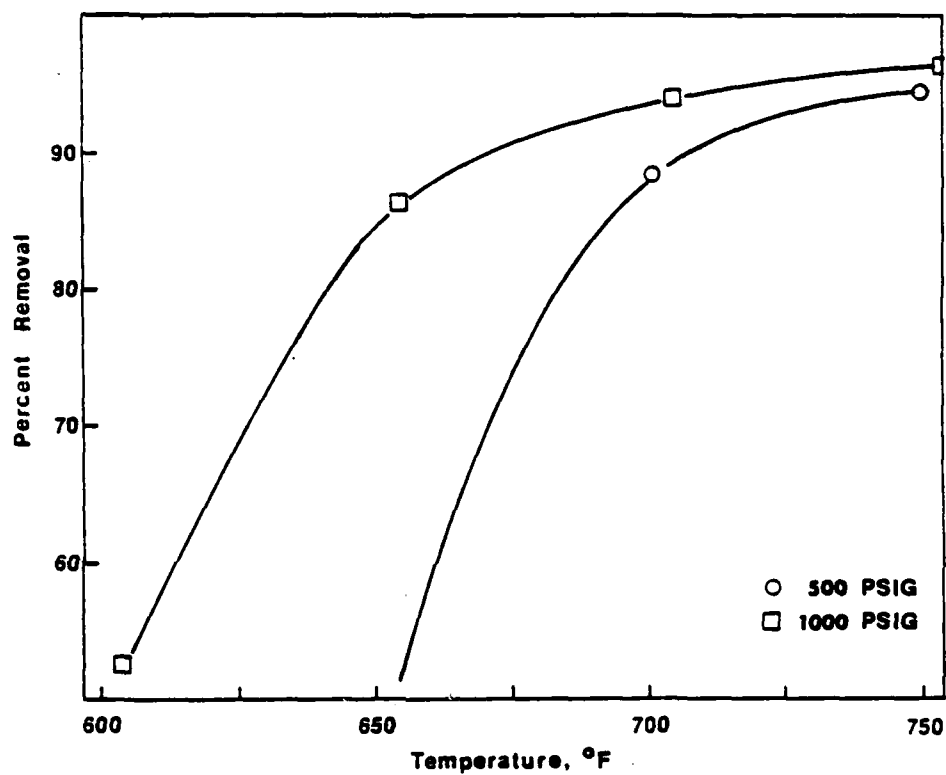


Figure III-2. Temperature Dependence Of Desulfurization At 2 LHSV Cobalt Molybdate Catalyst



**Figure III-3. In Situ Shale Oil Hydrotreating
Over Nickel Molybdate Catalyst: Temperature
Dependence Of Desulfurization At 2 LHSV**

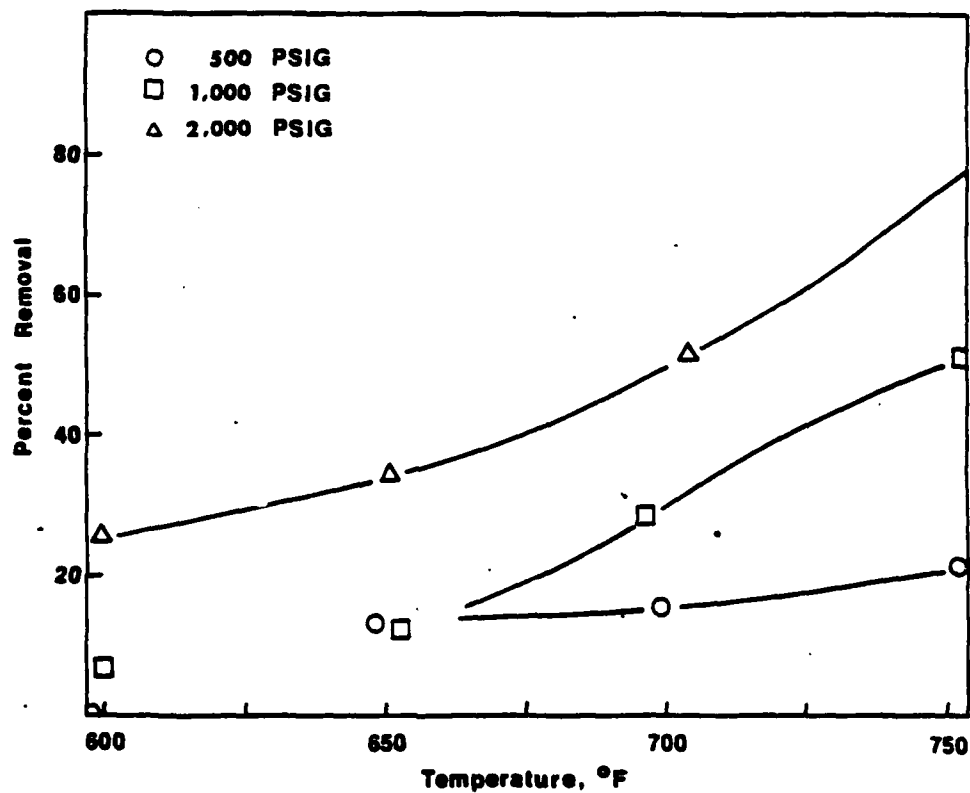


Figure III-4. Temperature Dependence Of Denitrogenation At 2 LHSV Cobalt Molybdate Catalyst

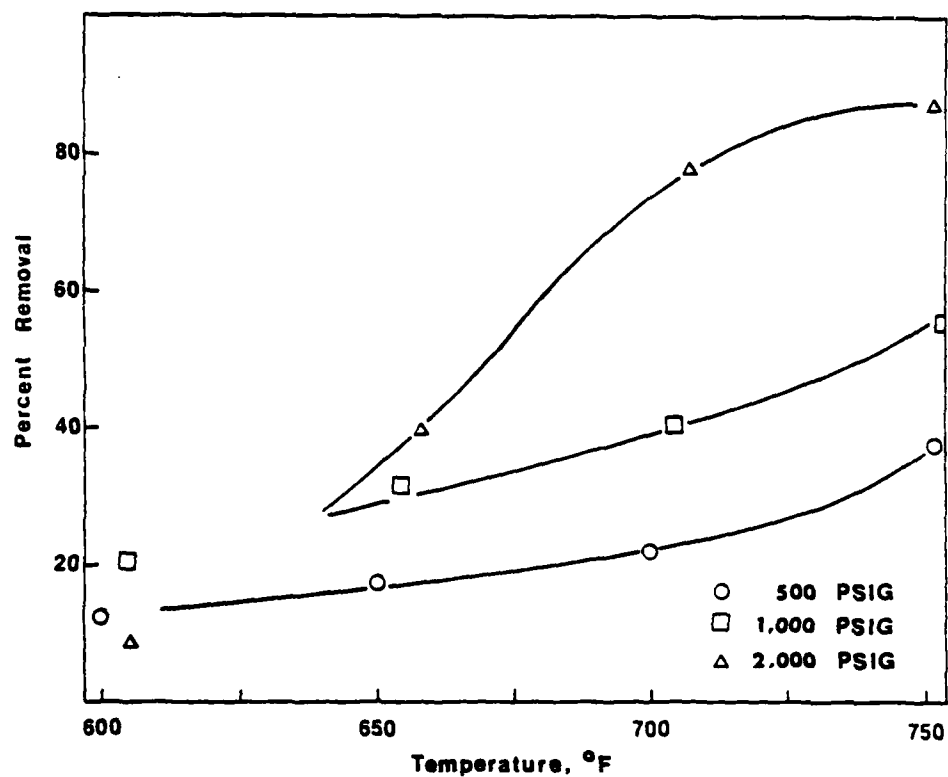
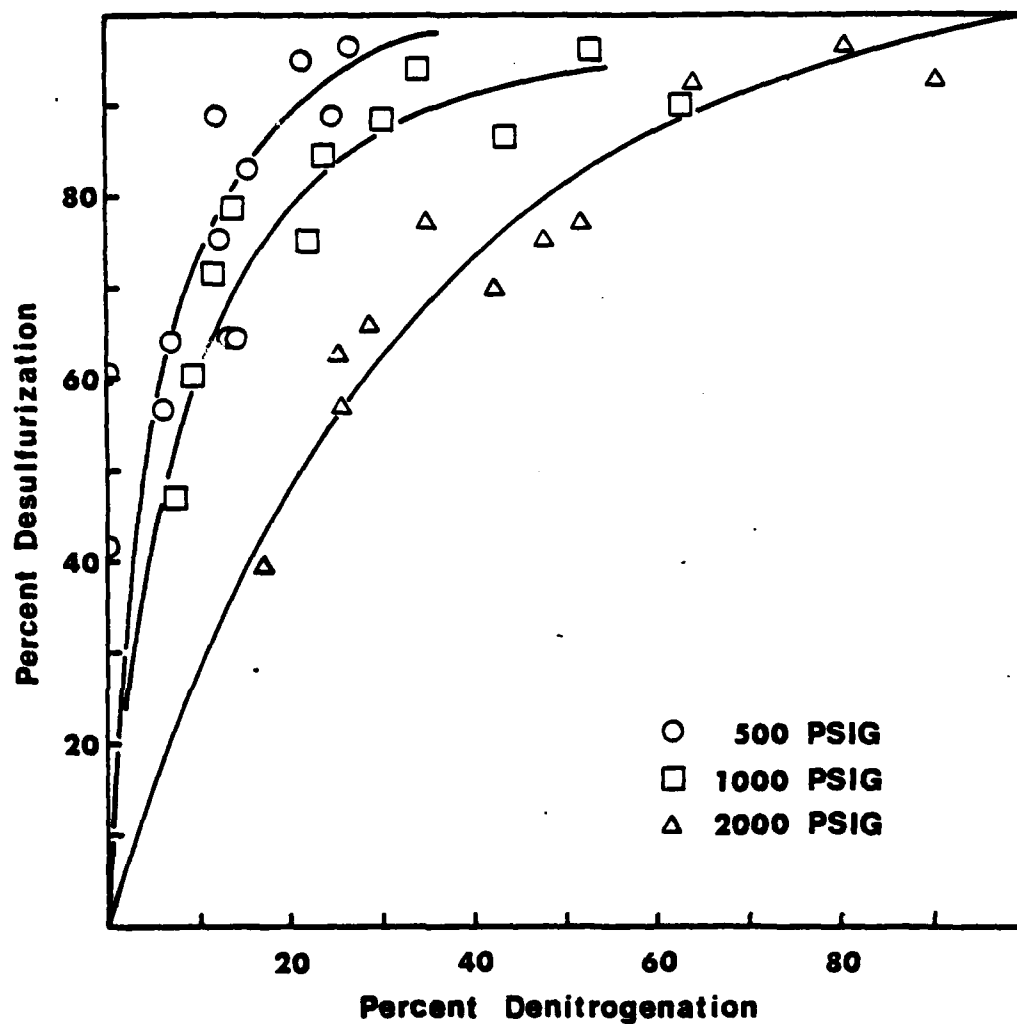


Figure III-5. In Situ Shale Oil Hydrotreating Over Nickel Molybdate Catalyst: Temperature Dependence Of Denitrogenation At 2 LHSV



**Figure III-6. In Situ Shale Oil Hydrotreating
Over Cobalt Molybdate Catalyst**

AD-A129 031

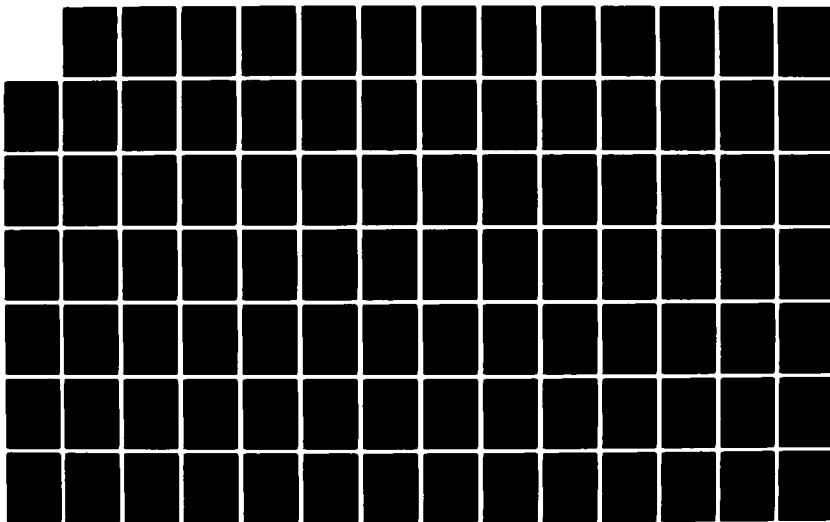
REFINING OF MILITARY JET FUELS FROM SHALE OIL PART II
VOLUME II (IN SITU..(U) ASHLAND PETROLEUM CO KY
H R MOORE ET AL. MAR 82 AFWAL-TR-81-2056-VOL-2-PT-2
F33615-78-C-2080

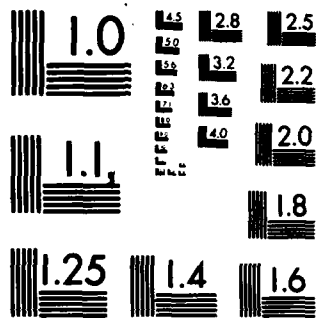
23

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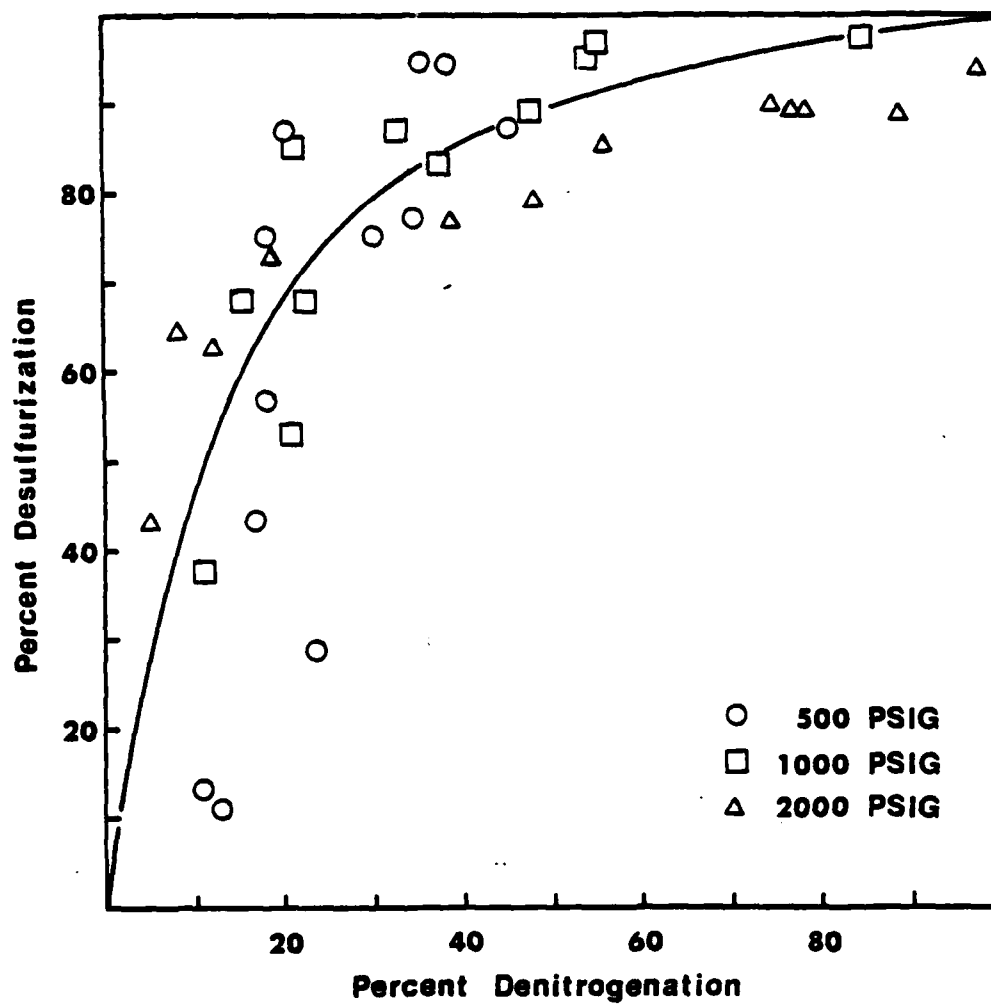
F/G 21/4

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A



**Figure III-7. In Situ Shale Oil Hydrotreating
Over Nickel Molybdate Catalyst**

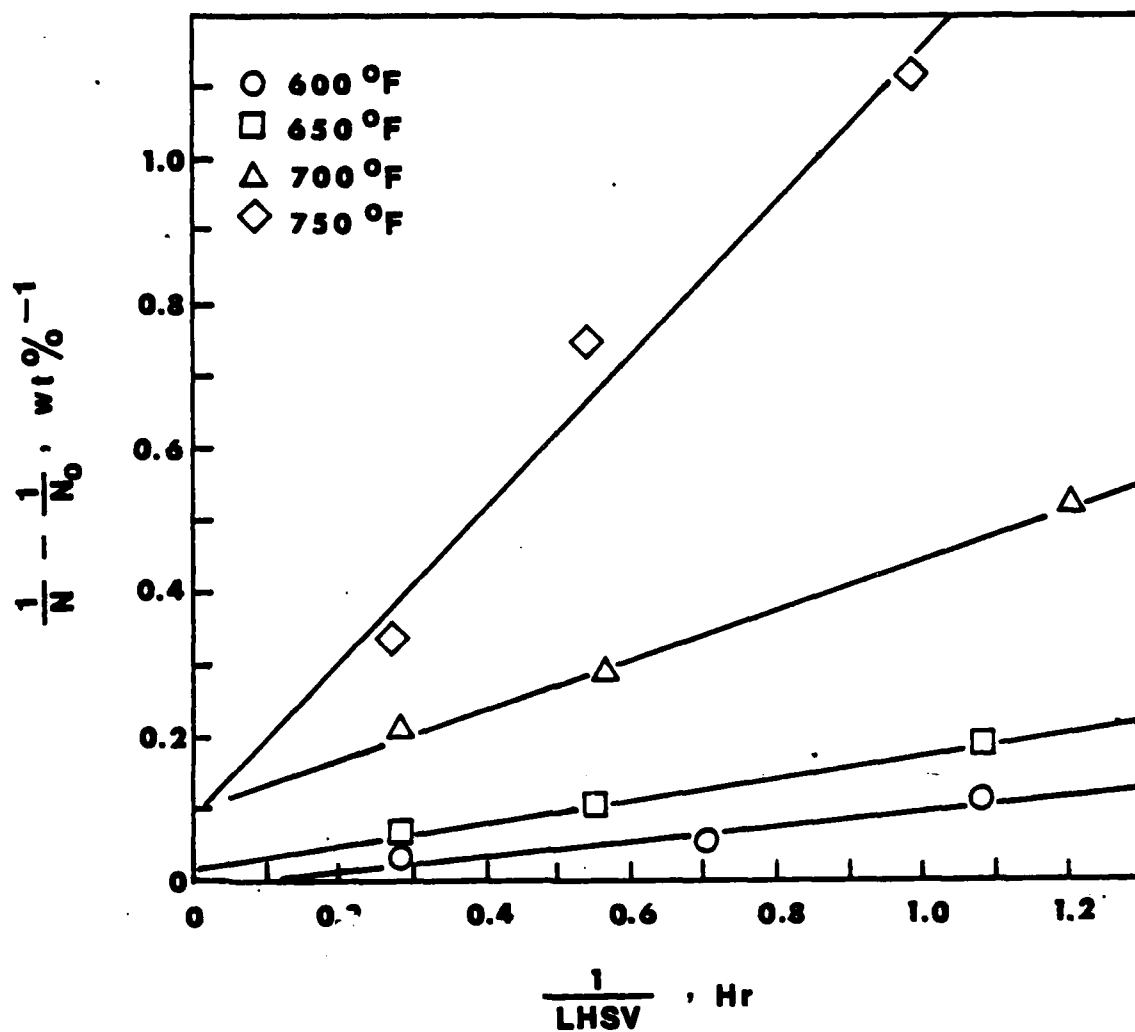


Figure III-8. Second Order Space Velocity Response Of Denitrogenation At 1000 PSIG Pressure Over Cobalt Molybdate Catalyst

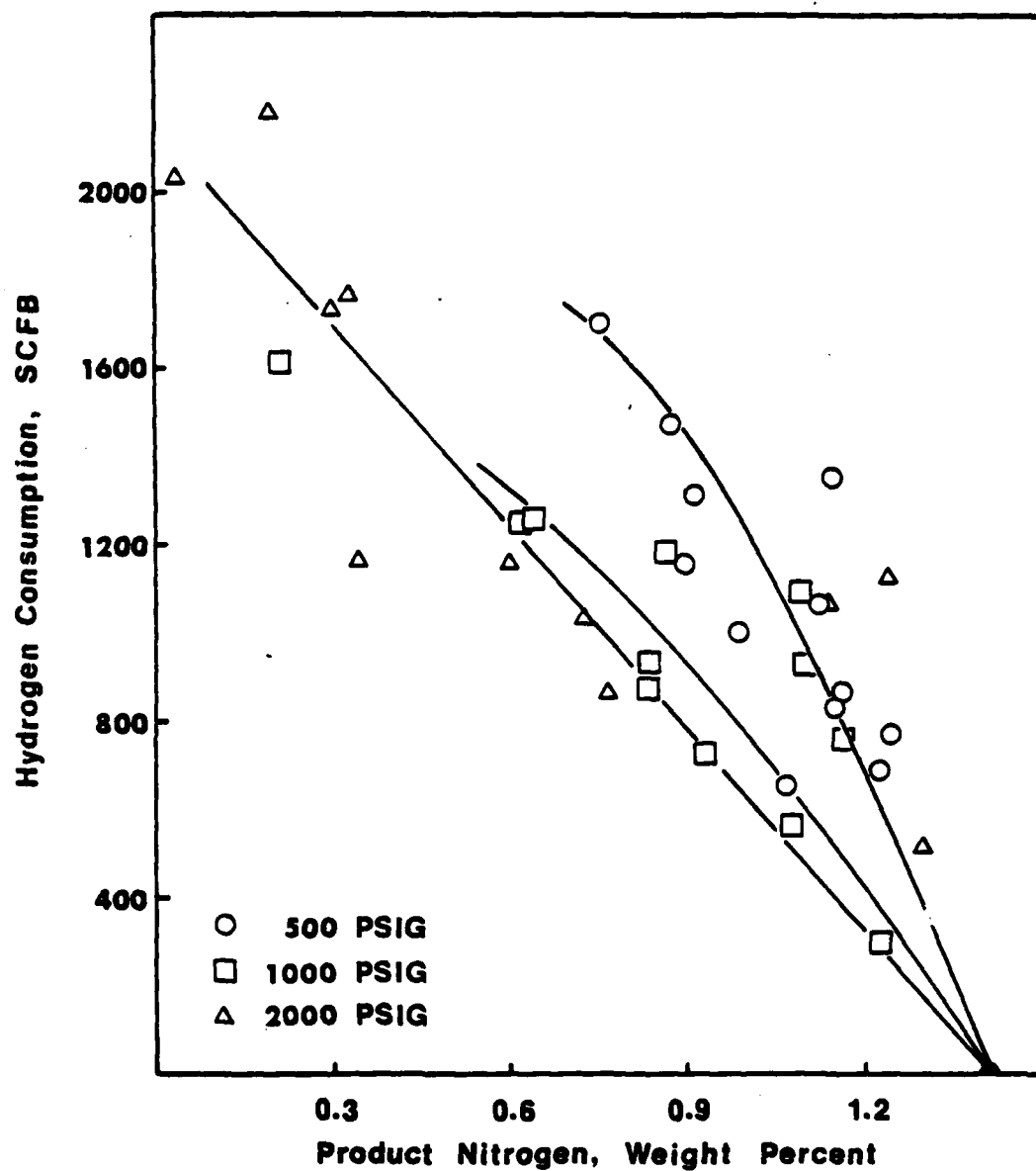


Figure III-9. In Situ Shale Oil Hydrotreating Over Nickel Molybdate Catalyst: Hydrogen Consumption Trends

removals at lower apparent hydrogen consumption. For both catalysts, approximately 70 hours of operation were required for (apparent) equilibration of catalyst activity.

OBJECTIVES

Objectives for these runs were: (1) examine initial catalyst stability parameters with respect to heteroatom removal, (2) determine the apparent time required for catalyst equilibration, (3) produce comparative data for cobalt molybdate and nickel molybdate catalysts and (4) produce adequate quantities of products for further processing and detailed evaluation.

UNIT DESCRIPTION

Nominal 1" I.D. trickle-flow reactors, described in Section I, were used for the M-11 study (cobalt molybdate catalyst). No external guardbed was used, as an internal tabular alumina preheat section provided this purpose.

Run M-12 was also performed on nominal 1" hydrotreating systems, but with a slightly different configuration. These systems are described in detail in Section VII.

EXPERIMENTAL

Raw in situ shale oil was hydrotreated at constant targeted conditions of 650°F, 2 LHSV, 3000 SCFB hydrogen circulation and 1000 psig total system pressure for both units. The charge was not filtered or pretreated in any way.

For run M-11 the reactor was packed to within 33.75" of reactor inlet with tabular alumina as postheat, onto which an 18.75" bed of 150-ml of 1/8" Co/Mo catalyst void-filled with 150-ml of Ottawa sand was added. The remaining space in the reactor was then filled with tabular alumina as preheat.

Run M-12 was accomplished with a slightly smaller reactor which was charged with 90-ml of nickel molybdate catalyst. Packing and void-filling procedures were followed in a manner analogous to that used for run M-11.

Pressure testing was accomplished to 1500 psig with nitrogen and hydrogen, after which the catalyst was sulfided to 700°F with H₂S at bottle pressure for four hours. The unit was cooled and purged of H₂S with flowing hydrogen, the hydrogen flow rate set and the unit pressured to 1000 psig.

Samples from each material balance period were stabilized by heating under vacuum to 300°F for at least two hours. This method proved most effective at removing entrained water from the sample. Stabilized samples were submitted for total nitrogen and sulfur analysis. Material balances were performed every twelve hours early in each run and at 24-hour intervals thereafter.

Hydrotreated product from run M-11 was composited in bulk, mixed thoroughly and split into halves. Each half was fractionated on a batch still: one half to a 500°F nominal cut point and the other to a 600°F cut point, producing samples M-111 and M-112, respectively.

Product from run M-12 was also composited and fractionated at 600°F atmospheric equivalent on the batch still to produce sample M-121.

FEEDSTOCK

Sufficient raw in situ shale oil was mixed and withdrawn from drum #06-SH-95-01 and supplied to lab personnel as feed to hydrotreating runs M-11 and M-12. The raw oil was obtained from the original 96-drum Air Force shipment and its properties are shown in Table III-26.

RESULTS

Hydrotreating material balances for both runs are shown in Tables III-27 and III-30. Fractionation of the products and the detailed analysis of each is delineated in Tables III-28, III-29 and III-31. The reader should note that oxygen balances are calculated, based on data obtained during Part 1 and Part 3 of this section, and are not measured values.

DISCUSSION

Both runs were stable over approximately 100 hours of operation. Figures III-10 and III-11 show material balance sample data versus time on stream, not including a nominal eight hour break-in and lineout period. Some scatter is noted in the M-12 denitrogenation data in particular, but overall results are reasonably smooth. Two intriguing trends show in both data sets: initial operation (hours

TABLE III-26

**M-SERIES HYDROTREATING FEED PROPERTIES
OF OCCIDENTAL IN SITU SHALE OIL**

| | |
|-----------------|------|
| Gravity, °API | 23.7 |
| Sulfur, Wt. % | 0.53 |
| Nitrogen, Wt. % | 1.42 |
| Oxygen, Wt. % | 1.21 |

TABLE III-27

CRUDE SHALE OIL HYDROTREATING

SERIES M-11

| Period | 1 | 2 | 3 | 4 | 5 | Total |
|-----------------------------|---------|---------|---------|---------|---------|---------|
| OPERATING CONDITIONS | | | | | | |
| Temperature, °F | 652 | 651 | 651 | 651 | 651 | 651 |
| Pressure, PSIG | 1027 | 1031 | 2031 | 1024 | 1025 | 1028 |
| LHSV, Hr ⁻¹ | 1.90 | 1.76 | 1.67 | 1.78 | 1.79 | 1.78 |
| H ₂ Rate, SCFB | 3149 | 3384 | 3614 | 3403 | 3301 | 3370 |
| MATERIAL BALANCE | | | | | | |
| Weight Percent of Feed | | | | | | |
| Feed | 100 | 100 | 100 | 100 | 100 | 100 |
| H ₂ In | 5.21 | 5.59 | 5.97 | 5.62 | 5.46 | 5.61 |
| Subtotal In | 105.21 | 105.59 | 105.97 | 105.62 | 105.46 | 105.61 |
| H ₂ O | (0.84) | (0.85) | (0.84) | (0.83) | (0.83) | (0.84) |
| NH ₃ | (0.52) | (0.45) | (0.53) | (0.56) | (0.49) | (0.46) |
| H ₂ S | (0.33) | (0.32) | (0.39) | (0.40) | (0.37) | (0.39) |
| H ₂ Out | 4.28 | 4.07 | 4.25 | 4.25 | 4.28 | 4.24 |
| C ₁ | - | - | - | - | - | - |
| C ₂ | 0.05 | 0.08 | 0.26 | 0.01 | 0.01 | 0.09 |
| C ₃ | 0.04 | 0.06 | 0.19 | 0.01 | 0.08 | 0.08 |
| C ₄ | 0.03 | 0.10 | 0.04 | - | 1.00 | 0.28 |
| C ₅ | 0.03 | - | - | - | - | 0.01 |
| Stabilized Liquid | 96.51 | 94.70 | 95.70 | 98.77 | 98.91 | 97.25 |
| Subtotal | 102.63 | 100.63 | 102.2 | 104.83 | 105.97 | 103.64 |
| Closure | 97.5 | 95.3 | 96.4 | 99.3 | 100.5 | 98.1 |
| Hydrogen Consumption, SCFB | 559 | 923 | 1042 | 829 | 709 | 828 |
| PRODUCT PROPERTIES | | | | | | |
| °API | 27.1 | 27.1 | 27.0 | 26.7 | 26.7 | 26.9 |
| Sulfur, Wt % | 0.23 | 0.24 | 0.17 | 0.16 | 0.18 | 0.17 |
| Nitrogen, Wt % | (1.011) | (1.088) | (1.008) | (0.950) | (1.008) | (1.056) |
| Oxygen, Wt % | - | - | - | - | - | (0.47) |

() - Calculated

TABLE III-28

CRUDE SHALE OIL HYDROTREATING
SERIES M-11
PRODUCT FRACTIONATION M-111

| Fraction, °F | IBP-500 | 500 + |
|-----------------------------|---------|--------|
| Yield, Wt % of Feed | 17.7 | 79.2 |
| Yield, LV % of Feed | 20.0 | 80.5 |
| °API | 43.5 | 26.2 |
| Carbon, Wt % | 84.98 | 86.90 |
| Hydrogen, Wt % | 12.98 | 11.43 |
| Nitrogen, Wt % | (1.07) | (1.01) |
| Basic Nitrogen, Wt % | 1.077 | 0.887 |
| Sulfur, Wt % | 0.11 | 0.17 |
| Oxygen, Wt % | - | - |
| Phenols, Wt % | - | - |
| Ramsbottom Carbon | - | 1.06 |
| Paraffins (P+N), LV % | (76.2) | - |
| Olefins, LV % | 12.0 | - |
| Naphthenes, LV % | - | - |
| Aromatics, LV % | 11.8 | - |
| Gross Heating Value, Btu/lb | 19,720 | 19,068 |
| | | |

TABLE III-29

CRUDE SHALE OIL HYDROTREATING

SERIES M-11

PRODUCT FRACTIONATION M-112

| Fraction, °F | IBP-600 | 600 + |
|-----------------------------|---------|--------|
| Yield, Wt % of Feed | 36.53 | 60.72 |
| Yield, LV % of Feed | 39.5 | 60.0 |
| °API | 36.8 | 22.4 |
| Carbon, Wt % | 85.84 | 86.65 |
| Hydrogen, Wt % | 12.51 | 11.70 |
| Nitrogen, Wt % | (1.15) | (1.09) |
| Basic Nitrogen, Wt % | 0.942— | 0.816 |
| Sulfur, Wt % | 0.10 | 0.17 |
| Oxygen, Wt % | - | - |
| Phenols, Wt % | - | - |
| Ramsbottom Carbon | - | 1.34 |
| Paraffins (P+N), LV % | (71.1) | - |
| Olefins, LV % | 9.4 | - |
| Naphthenes, LV % | - | - |
| Aromatics, LV % | 19.5 | - |
| Gross Heating Value, Btu/lb | 19,321 | 18,977 |
| | | |

TABLE III-30

CRUDE SHALE OIL HYDROTREATING SERIES M-12

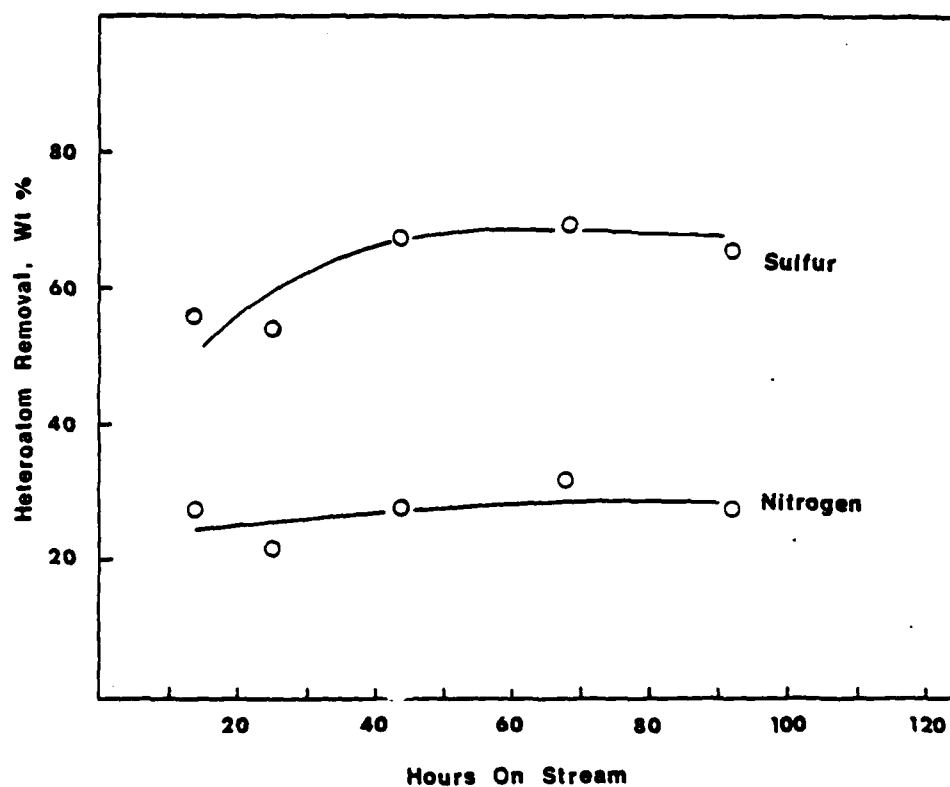
| Period | 1 | 2 | 3 | 4 | 5 | Total |
|-----------------------------|---------|---------|---------|---------|---------|--------|
| OPERATING CONDITIONS | | | | | | |
| Temperature, °F | 647 | 650 | 651 | 650 | 649 | 649 |
| Pressure, PSIG | 1000 | 1000 | 1010 | 1010 | 1022 | 1008 |
| LHSV, Hr ⁻¹ | 2.04 | 2.01 | 2.04 | 1.98 | 1.96 | 2.01 |
| H ₂ Rate, SCFB | 2950 | 2992 | 2944 | 3033 | 3064 | 2997 |
| MATERIAL BALANCE | | | | | | |
| Weight Percent of Feed | | | | | | |
| Feed | 100 | 100 | 100 | 100 | 100 | 100 |
| H ₂ In | 4.90 | 4.97 | 4.90 | 5.12 | 5.09 | 5.00 |
| Subtotal In | 104.90 | 104.97 | 104.90 | 105.12 | 105.09 | 105.00 |
| H ₂ O | (0.81) | (0.82) | (0.82) | (0.81) | (0.81) | (0.81) |
| NH ₃ | (0.68) | (0.34) | (0.46) | (0.57) | (0.45) | (0.50) |
| H ₂ S | (0.40) | (0.42) | (0.41) | (0.43) | (0.43) | (0.42) |
| H ₂ Out | 3.99 | 4.02 | 4.00 | 4.19 | - | 4.05 |
| C ₁ | - | - | - | - | - | - |
| C ₂ | 0.07 | 0.16 | 0.06 | 0.08 | - | 0.09 |
| C ₃ | 0.05 | 0.14 | 0.05 | 0.08 | - | 0.08 |
| C ₄ | 0.06 | 0.13 | 0.03 | 0.07 | - | 0.07 |
| C ₅ | 0.02 | 0.21 | 0.04 | 0.08 | - | 0.09 |
| Stabilized Liquid | 97.97 | 96.94 | 95.81 | 97.34 | 97.25 | 97.06 |
| Subtotal | 104.05 | 103.18 | 101.68 | 103.65 | - | 103.17 |
| Closure | 99.2 | 98.3 | 96.9 | 98.6 | - | 98.3 |
| Hydrogen Consumption, SCFB | 545 | 573 | 542 | 511 | - | 573 |
| PRODUCT PROPERTIES | | | | | | |
| °API | 27.3 | 27.3 | 27.2 | 27.3 | 27.3 | 27.3 |
| Sulfur, Wt % | 0.16 | 0.14 | 0.15 | 0.13 | 0.13 | 0.14 |
| Nitrogen, Wt % | (0.856) | (1.153) | (1.068) | (0.953) | (1.061) | (1.02) |
| Oxygen, Wt % | - | - | - | - | - | (0.4) |

() - Calculated

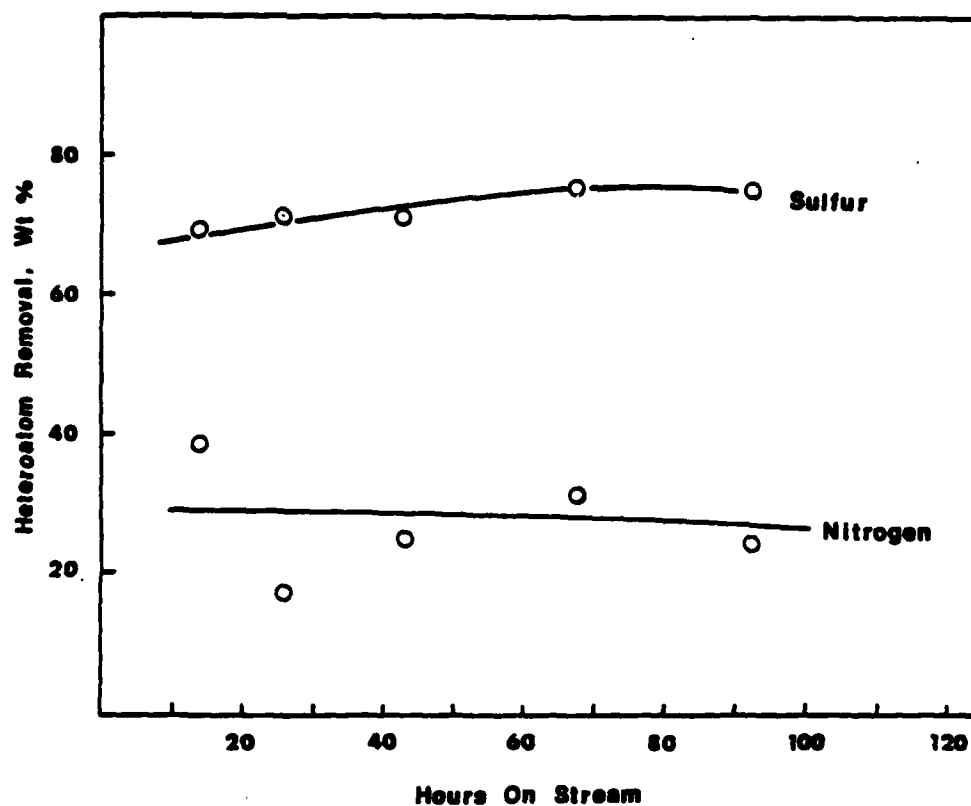
TABLE III-31

CRUDE SHALE OIL HYDROTREATING
SERIES M-12
PRODUCT FRACTIONATION M-121

| Fraction, °F | IBP-600 | 600 + |
|------------------------------------|----------------|--------------|
| Yield, Wt % of Feed | 32.1 | 65.0 |
| Yield, LV % of Feed | 34.4 | 65.0 |
| °API | 35.0 | 23.9 |
| Carbon, Wt % | 85.68 | 87.82 |
| Hydrogen, Wt % | 13.23 | 11.31 |
| Nitrogen, Wt % | (1.03) | (1.02) |
| Basic Nitrogen, Wt % | 0.887 | 0.737 |
| Sulfur, Wt % | 0.09 | 0.14 |
| Oxygen, Wt % | - | - |
| Phenols, Wt % | - | - |
| Ramsbottom Carbon | - | 1.53 |
| Paraffins (P+N), LV % | (71.1) | - |
| Olefins, LV % | 6.8 | - |
| Naphthenes, LV % | - | - |
| Aromatics, LV % | 22.1 | - |
| Gross Heating Value, Btu/lb | 19,286 | 18,938 |
| | | |



**Figure III-10. Heteroatom Removal Stability:
Crude Shale Oil Hydrotreating - Series M-11**



**Figure III-11. Heteroatom Removal Stability:
Crude Shale Oil Hydrotreating - Series M-12**

10-20) were followed by a data point of lower apparent activity, then followed by a period of gradually increasing activity. This increasing activity continued for both samples until apparent heteroatom removal peaked in the region of seventy hours on-stream. The data is of particular interest because these runs were performed independently by two different groups, on two different sets of equipment, without knowledge of the results from the other lab. The relative agreement between the first data point and the 70-hour data tends to confirm the parameter variation studies as valid for screening purposes.

The nickel molybdate catalyst appears to provide higher heteroatom removal at lower hydrogen consumption. One factor involved may have been the lower actual space velocity used in the cobalt molybdate runs. Detailed examination of the data indicates, however, that the probable cause was a malfunctioning gas meter. Weighted average hydrogen content of the cobalt molybdate product is 12.00 versus 11.94 for the nickel molybdate product (by hydrogen analyses), which, when given the similar gas production, indicates an erroneously high apparent hydrogen consumption for the M-11 data.

A further interesting observation is that the nitrogen content for the distillate (I-600°F) is higher than for the bottoms product in both runs.

3. CRUDE SHALE HYDROTREATER AGING

SUMMARY

A nominal 1-inch I.D. trickle flow reactor, packed with cobalt molybdate hydrotreating catalyst and provided with parallel guardbeds for arsenic removal, was operated for a period of 28 days (677 total hours) with crude in situ shale oil feedstock. Results from this run showed good stability, particularly in light of several operating upsets which occurred. This run successfully demonstrated the ability of the crude shale hydrotreater to operate for extended periods at low to moderate total pressure.

OBJECTIVES

Objectives for this run were to: (1) demonstrate catalyst stability, in particular, for sulfur removal and hydrogen consumption, over an extended period of time, (2) confirm earlier results obtained at shorter lineout and run lengths and (3) produce adequate quantities of products for both detailed analyses and further processing.

UNIT DESCRIPTION

The 1" nominal laboratory reactor utilized for this study has been adequately described in the earlier sections of this chapter. Due to the planned duration of the run, the reactor system was modified as shown in Figure III-12 to include parallel guardbeds for catalyst protection. The guardbeds were installed to allow independent operation, with the capability of replacing either unit while the

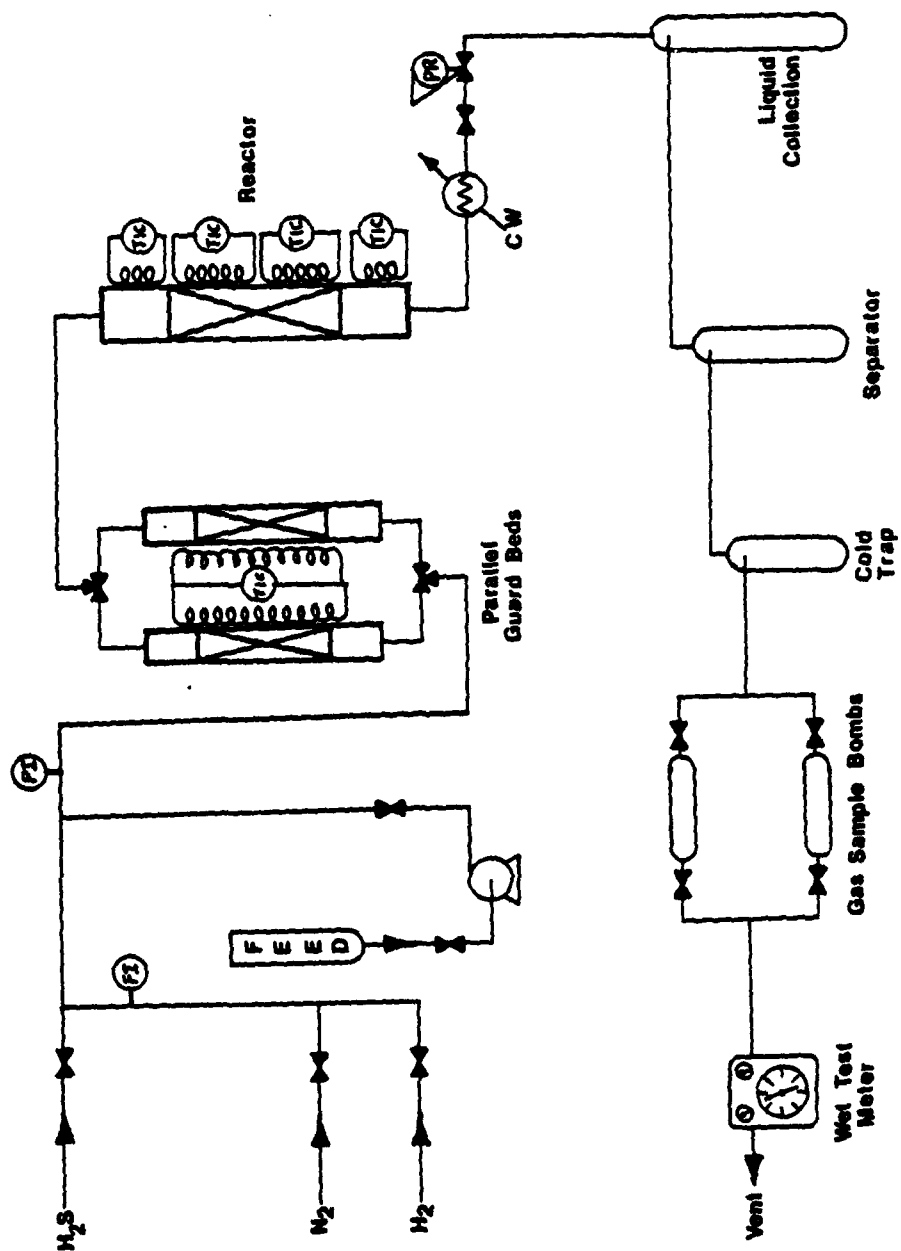


Figure III-12. Modified Crude Shale Hydrotreater For 30-Day Runs

other was on stream. The guardbeds were operated upflow, with both hydrogen and feedstock flowing through the unit. Pressure control was provided through the reactor outlet pressure control valve, allowing the capability to take any pressure drop across the guardbed(s) necessary up to the maximum discharge pressure capabilities of the pump. Temperature control was provided by an external heating tape and PID controller, driven by external skin temperature thermocouples.

FEEDSTOCK

All feedstock for this run was from a single, reserved drum of in situ shale oil supplied by the Air Force. The drum, coded #06-SH-94-01, was heated to approximately 100°F by a drum heater and five gallon samples were removed when necessary to replenish the operating supply. No dewatering or other pre-processing was practiced. Properties of the feed drum, taken for a well mixed grab sample from the full drum, are shown in Table III-32.

EXPERIMENTAL

Sample #06-SH-94-01 Occidental crude shale oil was hydrotreated at nominal conditions of 675°F, 1000 psig, 2.00 LHSV and 3000 SCFB hydrogen circulation by the Synthetic Oils Research Group.

The reactor was packed first with inert tabular alumina to a distance 33-7/8" from the reactor inlet. The catalyst bed consisted of 100-ml (72.3g) of catalyst and

TABLE III-32

CRUDE SHALE HYDROTREATER AGING
OCCIDENTAL CRUDE OIL (06-SH-94-01)
FEED PROPERTIES

| | |
|----------------------------|-------|
| Gravity, °API | 23.5 |
| Simulated Distillation, °F | |
| IBP | 344 |
| 10% | 470 |
| 50% | 672 |
| 90% | 874 |
| EP | 950 |
| Elemental, Wt. % | |
| Hydrogen | 11.7 |
| Sulfur | 0.64 |
| Total nitrogen | 1.41 |
| Oxygen | 1.13 |
| Fe, ppm | 71 |
| Ni, ppm | 13 |
| Va, ppm | 2 |
| As, ppm | 39 |
| Cl, ppm | 23.9 |
| Ramsbottom Carbon, Wt. % | 1.40 |
| Basic Nitrogen | 0.875 |
| Color | 8+ |
| Paraffins, Wt. % | 22.1 |
| Naphthenes, Wt. % | 31.6 |
| Aromatics, Wt. % | 46.3 |

100-ml of Ottawa sand. The sand and catalyst were added alternately in 10-ml increments to a level of 19" from the reactor inlet. The remaining preheat section, as measured from the reactor inlet, was tabular alumina to 11.75", activated alumina to 8.5" and the remaining space in the reactor was packed with tabular alumina. Thermocouples were located as follows: preheat at 47", upper bed at 42", lower bed at 34.5", post heat at 29", all with respect to the reactor outlet.

Following pressure testing to 1500 psig with nitrogen, then hydrogen, the catalyst was presulfided with H_2S at bottle pressure and 725°F for two hours. The reactor was allowed to cool nearly to room temperature with flowing hydrogen, hydrogen rate was set and the reactor was pressurized to 1000 psig. Feed was initiated and the entire system was slowly brought up to the desired operating conditions. The unit was lined out for 5.5 hours before the start of the first material balance period.

Two parallel guardbeds were installed in-line directly before the hydrotreater. The parallel arrangement provided the convenience of performing guardbed maintenance without interrupting unit operations. All oil and hydrogen which passed through the guardbed were controlled to maintain operating conditions of 500°F and reactor pressure, with a bed of 170-ml of 1/8" activated alumina. The beds were intended to remove arsenic, iron and other metals from the shale oil feed before entering the reactor preheat zone.

Conditions were monitored continuously and recorded hourly to maintain a 675°F bed temperature, 1000 psig reactor pressure, 2 LHSV and 3000 SCFB (3.77 SCF/Hr) hydrogen circulation.

From each (nominal 24 hour) material balance, a small sample was stripped at 300-350°F for at least two hours. The remaining product was combined into composite cans. Composites 1, 3, 5 and 7 were stabilized, and the stabilized product provided to the pilot plant to be cracked on the FCR unit.

RESULTS

A chronological description of the run is shown in Table III-33. The major problem encountered during the run was pump failure.

Operating results are shown in Table III-34 and Figures III-13 and III-14. Note that the reactor temperature is an hourly average temperature of the upper and lower portions of the bed, for each 24 hour period. Also, reactor pressure is an average pressure of the reactor inlet and outlet for the same duration of time.

Product fractionations were performed on small grab samples of several composite cans. These results are presented in Tables III-35, III-36 and III-37. Analysis of reactor catalyst bed and preheat alumina can be seen in Table III-38.

TABLE III-33

CHRONOLOGICAL RUN DESCRIPTION

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|------------------|---|
| 10/5/79 | 0525 | Start material balance - period 1 |
| | 0725-1030 | Difficulty maintaining constant H ₂ flow |
| | 1037 | By-passed H ₂ flow sight glass to stabilize H ₂ flow rate |
| | 1050 | Guardbed reactor 490°F at top |
| | 2330 | Repair pump |
| 10/6/79 | 0525 | End material balance - period 1 |
| | 0525 | Begin material balance - period 2 |
| 10/7/79 | 0525 | End material balance - period 2 |
| | 0525 | Begin material balance - period 3 |
| 10/8/79 | 0525 | End material balance - period 3 |
| | 0525 | Begin material balance - period 4 |
| 10/9/79 | 0525 | End material balance - period 4 |
| | 0525 | Begin material balance - period 5 |
| | 1225 | Plug in cold trap causing wet test meter to malfunction |
| | 1545-2100 | Cold trap center post plugged causing high separator pressure |
| 10/10/79 | 0525 | End material balance - period 5 |
| | 0525 | Begin material balance - period 6 |
| | 0740 | Plug in cold trap causing gas readings to be low |
| | 1820 | Priming adjustment valve fell off and pump rate took off |
| 10/11/79 | 0525 | End material balance - period 6 |
| | 0525 | Begin material balance - period 7 |
| | 0525 | Pump failed to maintain feed rate |
| | 0525 | Feed buret broken |
| | 0825 | Pump stopped |
| | 0905 | Pump stopped |
| | 1200 | Feed buret leaking |
| | 1800 | Hydrogen rate fluctuating |
| | 1820 | Switched guard beds |
| | 1920-2225 | Pump lost prime |

TABLE III-33 (CONT'D)

CHRONOLOGICAL RUN DESCRIPTION

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|------------------|---|
| 10/12/79 | 0430 | Vent valve fitting vibrated loose causing loss of pump |
| | 0525 | End material balance - period 7 |
| | 0525 | Begin material balance - period 8 |
| | 0735 | Off-gas rate low |
| | 1105 | Pump back on |
| | 1240-1255 | Pump down |
| 10/13/79 | 0045 | Switched guardbeds |
| | 0525 | End material balance - period 8 |
| | 0525 | Begin material balance - period 9 |
| | 0935 | Preheat temperature and bed temperature decreased |
| | 1230 | Pump stopped and replaced |
| | 1500 | Pump reprimed |
| 10/14/79 | 0430 | Pump replaced |
| | 0525 | End material balance - period 9 |
| | 0525 | Begin material balance - period 10 |
| 10/15/79 | 0525 | End material balance - period 10 |
| | 0525 | Begin material balance - period 11 |
| | 1325 | High level in sight glass |
| 10/16/79 | 0525 | End material balance - period 11 |
| | 0525 | Begin material balance - period 12 |
| | 0725 | Adjusted H ₂ rate |
| | 1335 | Added water to wet test meter to bring up to proper level |
| | 1825 | Water in product when drained |
| 10/17/79 | 0325 | Pump lost prime |
| | 0400 | Replaced pump |
| | 0445 | Replaced second pump |
| | 0525 | End material balance - period 12 |
| | 0525 | Begin material balance - period 13 |
| 10/18/79 | 0525 | End material balance - period 13 |
| | 0525 | Begin material balance - period 14 |

TABLE III-33 (CONT'D)

CHRONOLOGICAL RUN DESCRIPTION

| DATE | TIME, HRS | ITEM |
|----------|-----------|---|
| 10/19/79 | 0525 | End material balance - period 14 |
| | 0525 | Begin material balance - period 15 |
| | 0525-0625 | Feed pump down |
| | 1325 | Feed pump lost prime |
| | 1400 | Pump replaced. Pump pressure got too high before opening feed valve. Pressure gauge reads extremely high |
| | 1825 | Pump stopped - replaced pump |
| | 2325 | Replaced second pump |
| 10/20/79 | 0525 | End material balance - period 15 |
| | 0525 | Begin material balance - period 16 |
| 10/21/79 | 0125-0450 | Extreme pressures were noted on pump pressure gauge. Hydrogen rate continues at an increased rate. Pump failed. No oil flowing; lines plugged. Guardbed temperatures shut off |
| | 0500 | Replaced leaking pump |
| | 0500 | Switched guardbeds |
| | 0825 | Pump lost prime |
| | 0925 | End material balance - period 16 |
| | 0925 | Begin material balance - period 17 |
| | 1245 | Pump lost prime |
| 10/22/79 | 0200 | Switch guardbeds |
| | 0525 | End material balance - period 17 |
| | 0525 | Begin material balance - period 18 |
| 10/23/79 | 0525 | End material balance - period 18 |
| | 0525 | Begin material balance - period 19 |
| | 0755 | Plug in inlet size of reactor |
| | 1000 | Pump lost prime |
| | 1845 | Pump lost prime |
| 10/24/79 | 0525 | End material balance - period 19 |
| | 0525 | Begin material balance - period 20 |
| | 0850 | Pump pumping pump oil through discharge. Replaced pump. Leak developed around feed buret bottom. New pump would not pump |
| | 1000-0025 | All temperatures decreased. Rebuilding pump |
| | 1545 | Feed line to guardbed replaced |
| | 2025 | End lineout of material balance - period 20 |
| | 2025 | Begin material balance - period 20 |

TABLE III-33 (CONT'D)

CHRONOLOGICAL RUN DESCRIPTION

| <u>DATE</u> | <u>TIME, HRS</u> | <u>ITEM</u> |
|-------------|------------------|---|
| 10/25/79 | 0525 | End material balance - period 20 |
| | 0525 | Begin material balance - period 21 |
| | 0825 | Plug in cold trap |
| | 1010 | Pump lost prime |
| | 1225 | Pump replaced |
| | 1325 | Exothermic reaction when feed was introduced |
| | 1800 | Pump replaced |
| 10/26/79 | 0525 | End material balance - period 21 |
| | 0525 | Begin material balance - period 22 |
| | 1040 | Pump leaking - replaced with two pumps |
| | 1040 | Rebuilt pump |
| | 1355 | Exothermic reaction - heater temperature decreased |
| | 1925-2015 | Pump failure - replaced vent screw |
| | 2015 | Screw head broke off |
| 10/27/79 | 2015 | Replaced pump |
| | 0250 | Replaced pump twice. Plugged suction piping |
| | 0525 | Pump ran dry |
| | 0530 | End material balance - period 22 |
| | 0530 | Begin material balance - period 23 |
| 10/28/79 | 0525 | End material balance - period 23 |
| | 0525 | Begin material balance - period 24 |
| 10/29/79 | 0525 | End material balance - period 24 |
| | 0525 | Begin material balance - period 25 |
| 10/30/79 | 0525 | End material balance - period 25 |
| | 0525 | Begin material balance - period 26 |
| | 2325 | Replace pump |
| | 2340 | Pump leaks around checks - removed and cleaned pump |
| 10/31/79 | 0525 | End material balance - period 26 |
| | 0525 | Begin material balance - period 27 |
| 11/1/78 | 0525 | End material balance - period 27 |
| | 0525 | Begin material balance - period 28 |
| | 1910 | Pump down |
| | 1925 | Replaced pump |
| 11/2/79 | 0525 | End material balance - period 28 shutdown |

TABLE III-34

| Period | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| OPERATING CONDITIONS | | | | | | | | | | | | |
| Temperature, °F | 680 | 677 | 672 | 677 | 677 | 676 | 676 | 667 | 678 | 678 | 678 | 679 |
| Pressure, PSIG | 1000 | 999 | 1005 | 1013 | 1020 | 1015 | 1008 | 1012 | 1016 | 1019 | 1031 | 1024 |
| LHSV, Hr ⁻¹ | 2.00 | 1.76 | 1.85 | 1.87 | 2.06 | 1.75 | 1.59 | 1.66 | 1.78 | 2.34 | 2.08 | 1.98 |
| Hydrogen Rate, SCFB | 2987 | 3403 | 3247 | 3248 | 2916 | 3412 | 3886 | 3654 | 3375 | 2569 | 2902 | 3025 |
| MATERIAL BALANCE | | | | | | | | | | | | |
| Weight Percent of Feed | | | | | | | | | | | | |
| Feed | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| Hydrogen In | 4.93 | 5.62 | 5.36 | 5.36 | 4.81 | 5.63 | 6.41 | 6.03 | 5.57 | 4.24 | 4.79 | 4.92 |
| Subtotal In | 104.93 | 105.62 | 105.36 | 105.36 | 104.81 | 105.63 | 106.41 | 106.03 | 105.57 | 104.24 | 104.79 | 104.99 |
| H ₂ O | (0.81) | (0.78) | (0.82) | (0.79) | (0.82) | (0.82) | (0.84) | - | (0.84) | (0.82) | (0.83) | (0.84) |
| H ₂ S | (0.53) | (0.52) | (0.53) | (0.52) | (0.55) | (0.46) | (0.52) | - | (0.58) | (0.52) | (0.48) | (0.50) |
| NH ₃ | (0.29) | (0.20) | (0.31) | (0.23) | (0.20) | (0.17) | (0.34) | - | (0.34) | (0.21) | (0.28) | (0.28) |
| Hydrogen Out | 3.26 | 3.75 | 3.65 | 4.06 | 3.96 | 4.13 | 5.25 | - | 4.26 | 3.35 | 3.66 | 4.07 |
| C ₁ | 0.64 | 0.58 | 0.14 | 0.03 | - | - | - | - | 0.02 | - | - | 0.11 |
| C ₂ | 0.24 | 0.30 | 0.34 | 0.02 | 0.07 | 0.20 | 0.70 | - | 1.42 | 0.40 | 0.40 | 0.28 |
| C ₃ | 0.24 | 0.25 | 0.27 | 0.03 | 0.06 | 0.15 | 0.78 | - | 1.03 | 0.36 | 0.23 | 0.26 |
| C ₄ | 0.16 | 0.05 | 0.07 | - | 0.05 | 0.77 | 1.20 | - | 0.14 | 1.84 | 0.10 | 0.11 |
| C ₅ | 0.05 | - | - | - | - | 0.03 | - | - | - | - | 0.03 | 0.06 |
| Stabilized Liquid | 101.52 | 108.58 | 100.67 | 105.92 | 99.35 | 99.34 | 94.86 | 98.63 | 94.89 | 100.41 | 97.15 | 95.71 |
| Subtotal Out, %wt | 107.74 | 115.01 | 106.80 | 111.60 | 105.06 | 106.27 | 104.49 | - | 103.52 | 107.91 | 103.16 | 102.22 |
| Closure, %wt | 102.7 | 108.9 | 101.4 | 105.9 | 100.2 | 100.6 | 98.2 | - | 98.1 | 103.5 | 98.4 | 97.4 |
| GAP | 27.4 | 27.7 | 27.8 | 28.3 | 27.7 | 27.4 | 27.4 | 27.1 | 27.4 | 27.6 | 27.2 | 27.5 |
| Sulfur, %wt | - | - | - | 0.14 | 0.12 | 0.18 | 0.16 | - | 0.10 | 0.15 | 0.19 | 0.18 |
| Nitrogen, %wt | - | - | - | (1.15) | (1.25) | (1.28) | (1.19) | - | (1.19) | (1.23) | (1.21) | (1.23) |
| Basic Nitrogen, %wt | - | - | - | 0.77 | - | 0.88 | 0.81 | - | - | 0.84 | - | - |
| Hydrogen Consumption, SCFB | 1013 | 1129 | 1036 | 786 | 519 | 912 | 706 | - | 797 | 541 | 687 | 562 |

() - Calculated

TABLE III-34 (Cont'd)

| Period | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 | 24 |
|----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| OPERATING CONDITIONS | | | | | | | | | | | | |
| Temperature, °F | 678 | 679 | 678 | 679 | 676 | 675 | 675 | 675 | 676 | 658 | 677 | 676 |
| Pressure, PSIG | 1016 | 1020 | 1027 | 1032 | 1006 | 1007 | 1014 | 1016 | 1011 | 1004 | 1020 | 1011 |
| LHSV, Hr ⁻¹ | 1.96 | 2.10 | 1.84 | 2.07 | 2.10 | 2.02 | 2.06 | 2.06 | 1.83 | 1.26 | 1.92 | 1.92 |
| Hydrogen Rate, SCFB | 3050 | 2899 | 3307 | 2939 | 2858 | 3017 | 2954 | 2943 | 3265 | 4773 | 3175 | 3153 |
| MATERIAL BALANCE | | | | | | | | | | | | |
| Weight Percent of Feed | | | | | | | | | | | | |
| Feed | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| Hydrogen In | 5.04 | 4.79 | 5.46 | 4.85 | 4.72 | 4.98 | 4.88 | 4.86 | 5.39 | 7.88 | 5.24 | 5.20 |
| Subtotal In | 105.04 | 104.79 | 105.46 | 104.85 | 104.72 | 104.98 | 104.88 | 104.86 | 105.39 | 107.88 | 105.24 | 105.20 |
| H ₂ O | (0.83) | (0.82) | (0.83) | - | (0.85) | (0.82) | (0.83) | (0.88) | (0.86) | - | (0.83) | (0.83) |
| H ₂ S | (0.48) | (0.47) | (0.48) | - | (0.47) | (0.51) | (0.54) | (0.53) | (0.53) | - | (0.51) | (0.50) |
| NH ₃ | (0.25) | (0.28) | (0.26) | - | (0.29) | (0.18) | (0.31) | (0.36) | (0.34) | - | (0.24) | (0.26) |
| Hydrogen Out | 3.96 | 4.01 | 4.54 | - | 3.60 | 3.94 | 3.72 | 3.90 | 3.88 | - | 3.79 | 3.81 |
| C ₁ | - | - | 0.07 | - | - | 0.07 | 0.12 | 0.18 | 0.06 | - | 0.01 | 0.20 |
| C ₂ | 0.81 | 0.15 | 0.07 | - | 0.12 | 0.07 | 0.16 | 0.07 | 0.24 | - | 0.01 | 0.05 |
| C ₃ | 0.05 | 0.11 | 0.04 | - | 0.11 | 0.05 | 0.10 | 0.06 | 0.26 | - | 0.34 | 0.04 |
| C ₄ | 0.83 | 0.11 | 0.03 | - | - | 0.03 | 0.07 | 0.05 | 0.19 | - | 0.27 | 0.08 |
| C ₅ | - | 0.03 | - | - | 0.03 | - | - | - | - | - | - | - |
| Stabilized Liquid | 98.89 | 101.07 | 98.6 | 98.75 | 93.10 | 105.00 | 96.39 | 87.22 | 90.57 | 106.96 | 97.52 | 97.14 |
| Subtotal Out, %wt | 106.10 | 107.05 | 104.92 | - | 98.57 | 110.67 | 102.24 | 93.25 | 96.93 | - | 103.52 | 102.91 |
| Closure, %wt | 101.0 | 102.2 | 99.5 | - | 94.1 | 105.4 | 97.5 | 88.9 | 92.0 | - | 98.4 | 97.8 |
| oAPI | 27.2 | 27.5 | 27.2 | 27.7 | 28.0 | 27.3 | 27.2 | 27.3 | 27.7 | 28.0 | 27.3 | 27.2 |
| Sulfur, %wt | 0.19 | - | 0.19 | - | 0.21 | 0.15 | 0.14 | 0.16 | 0.16 | - | 0.16 | 0.17 |
| Nitrogen, %wt | (1.22) | (1.17) | (1.21) | - | (1.26) | (1.20) | (1.20) | (1.28) | (1.25) | - | (1.24) | (1.23) |
| Basic Nitrogen, %wt | - | - | 0.83 | - | - | 0.83 | 0.87 | 0.85 | 0.85 | - | 0.86 | 0.86 |
| Hydrogen Consumption, SCFB | 652 | 469 | 560 | - | 675 | 632 | 698 | 579 | 917 | - | 878 | 844 |

() - Calculated

TABLE III-34 (Cont'd)

| Period | 25 | 26 | 27 | 28 | 29 | 30 |
|----------------------------|--------|--------|--------|--------|----|----|
| OPERATING CONDITIONS | | | | | | |
| Temperature, °F | 676 | 676 | 676 | 676 | | |
| Pressure, PSIG | 1012 | 1010 | 1018 | 1013 | | |
| LHSV, Hr ⁻¹ | 2.00 | 2.03 | 2.13 | 1.90 | | |
| Hydrogen Rate, SCFB | 3062 | 2992 | 2846 | 3206 | | |
| MATERIAL BALANCE | | | | | | |
| Weight Percent of Feed | | | | | | |
| Feed | 100.00 | 100.00 | 100.00 | 100.00 | | |
| Hydrogen In | 5.05 | 4.94 | 4.70 | 5.29 | | |
| Subtotal In | 105.05 | 104.94 | 104.70 | 105.29 | | |
| H ₂ O | (0.83) | (0.83) | (0.88) | - | | |
| H ₂ S | (0.49) | (0.51) | (0.55) | - | | |
| NH ₃ | (0.37) | (0.36) | (0.47) | - | | |
| Hydrogen Out | 4.02 | 3.74 | 3.67 | - | | |
| C ₁ | - | - | - | - | | |
| C ₂ | 0.50 | 0.31 | 0.50 | - | | |
| C ₃ | 0.43 | 0.26 | 0.45 | - | | |
| C ₄ | 0.77 | 0.13 | 1.07 | - | | |
| C ₅ | 0.22 | - | - | - | | |
| Stabilized Liquid | 97.85 | 96.06 | 86.09 | 98.51 | | |
| Subtotal Out, %wt | 105.48 | 102.20 | 93.68 | - | | |
| Closure, %wt | 100.4 | 97.4 | 89.5 | - | | |
| oAPI | 27.3 | 27.3 | 27.1 | 27.1 | | |
| Sulfur, %wt | 0.18 | 0.17 | 0.14 | 0.10 | | |
| Nitrogen, %wt | (1.13) | (1.16) | (1.19) | (1.29) | | |
| Basic Nitrogen, %wt | 0.87 | 0.86 | 0.88 | 0.88 | | |
| Hydrogen Consumption, SCFB | 625 | 727 | 622 | - | | |

() - Calculated

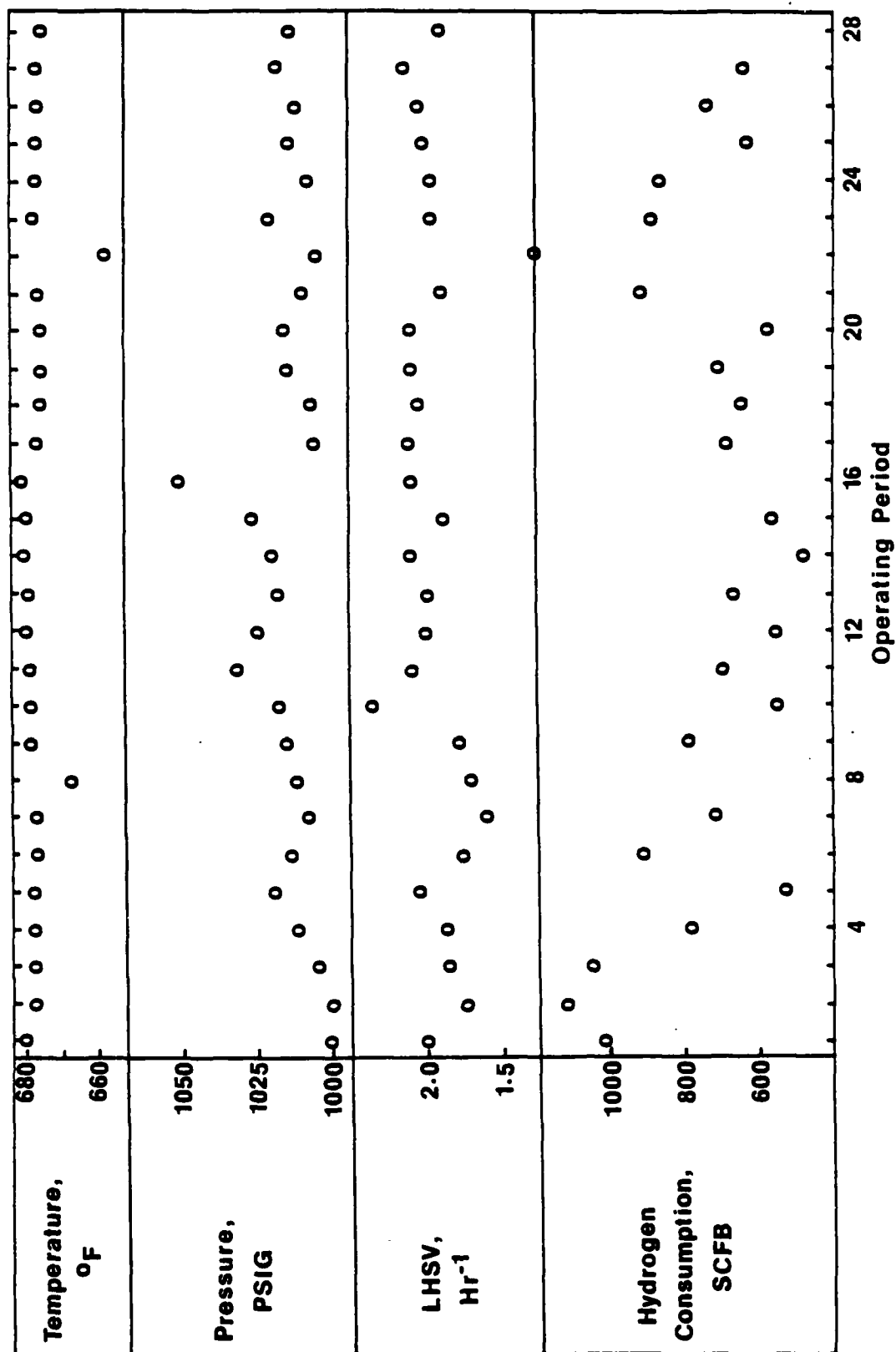


Figure III-13. CSHT Results For In Situ Shale Oil

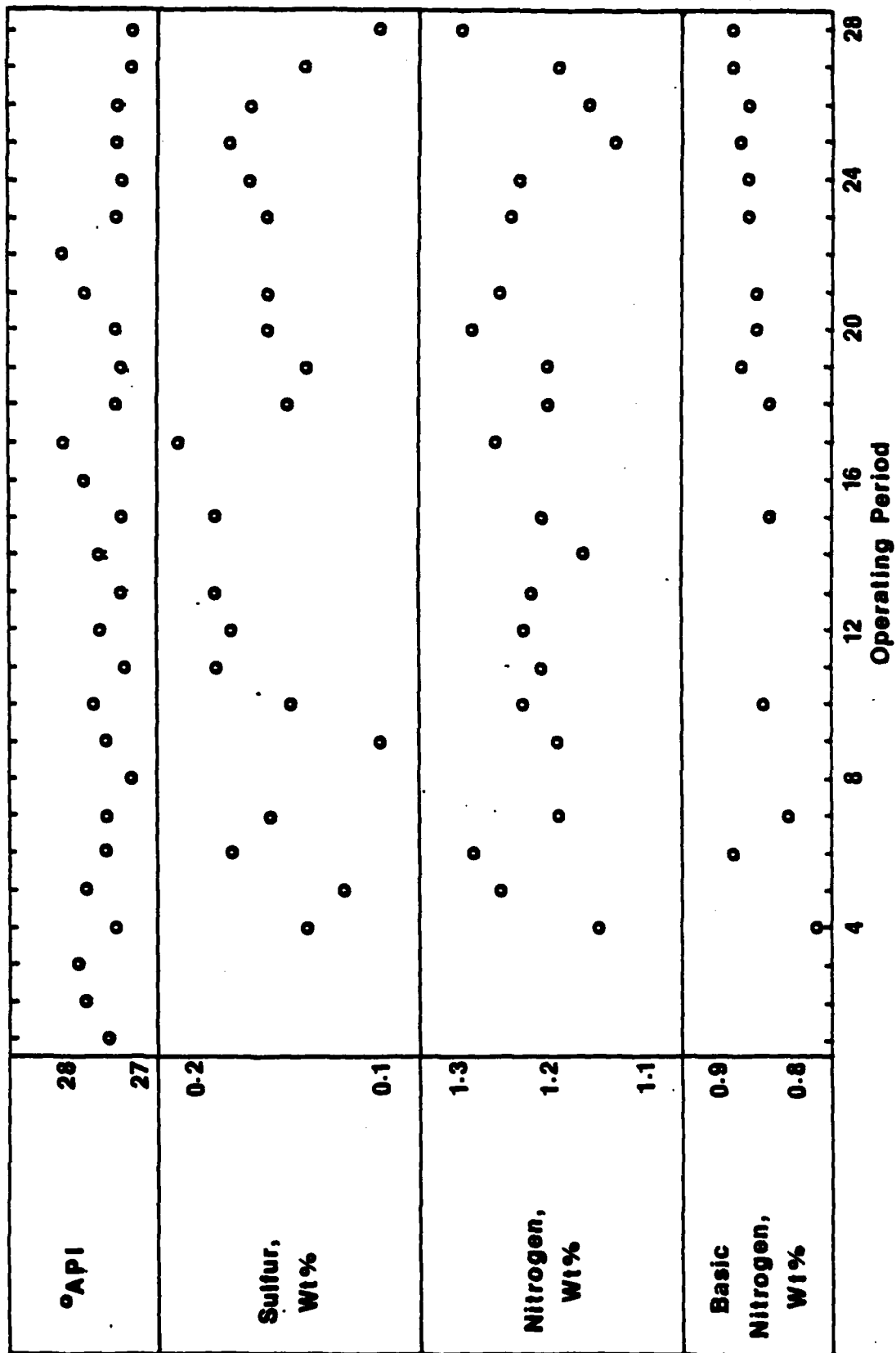


Figure III-14. CSHT Aging Results For In Situ Shale Oil

TABLE III-35

COMPOSITE PRODUCT INSPECTION
COMPOSITE 3
PERIODS 9-11

| Fraction, °F | -600 | + 600 |
|-----------------------------|-------|-------|
| Yield, Wt % of Feed | 33.0 | 64.5 |
| Yield, LV % of Feed | 35.6 | 64.9 |
| °API | 35.5 | 24.4 |
| Carbon, Wt % | - | - |
| Hydrogen, Wt % | 13.0 | - |
| Nitrogen, Wt % | ---- | ---- |
| Basic Nitrogen, Wt % | 0.975 | 0.821 |
| Sulfur, Wt % | 0.06 | 0.15 |
| Oxygen, Wt % | - | - |
| Phenols, Wt % | - | - |
| Ramsbottom Carbon | 0.23 | 0.93 |
| Paraffins (P+N), LV % | - | - |
| Olefins, LV % | - | - |
| Naphthenes, LV % | - | - |
| Aromatics, LV % | - | - |
| Gross Heating Value, Btu/lb | - | - |
| Arsenic, ppb | 11 | 5000 |

TABLE III-36

COMPOSITE PRODUCT INSPECTION
COMPOSITE 5
PERIODS 15-20

| Fraction, °F | -600 | + 600 |
|-----------------------------|--------|--------|
| Yield, Wt % of Feed | 32.5 | 64.0 |
| Yield, LV % of Feed | 35.1 | 64.1 |
| °API | 35.9 | 23.7 |
| Carbon, Wt % | — | — |
| Hydrogen, Wt % | 13.0 | — |
| Nitrogen, Wt % | (1.34) | (1.41) |
| Basic Nitrogen, Wt % | 0.962 | 0.962 |
| Sulfur, Wt % | 0.06 | 0.18 |
| Oxygen, Wt % | - | - |
| Phenols, Wt % | - | - |
| Ramsbottom Carbon | - | 0.99 |
| Paraffins (P+N), LV % | - | - |
| Olefins, LV % | - | - |
| Naphthenes, LV % | - | - |
| Aromatics, LV % | - | - |
| Gross Heating Value, Btu/lb | - | - |
| Arsenic, ppb | 10 | 5000 |

() - Calculated

TABLE III-37

COMPOSITE PRODUCT INSPECTION
COMPOSITE 7
PERIODS 25 - 28

| Fraction, °F | -600 | + 600 |
|-----------------------------|-------|-------|
| Yield, Wt % of Feed | 33.0 | 61.6 |
| Yield, LV % of Feed | 35.8 | 61.9 |
| °API | 36.5 | 24.2 |
| Carbon, Wt % | ---- | ---- |
| Hydrogen, Wt % | 12.9 | ---- |
| Nitrogen, Wt % | ---- | ---- |
| Basic Nitrogen, Wt % | 0.821 | 0.828 |
| Sulfur, Wt % | 0.07 | 0.16 |
| Oxygen, Wt % | - | - |
| Phenols, Wt % | - | - |
| Ramsbottom Carbon | 0.24 | 0.96 |
| Paraffins (P+N), LV % | ---- | ---- |
| Olefins, LV % | ---- | ---- |
| Naphthenes, LV % | ---- | ---- |
| Aromatics, LV % | ---- | ---- |
| Gross Heating Value, Btu/lb | ---- | ---- |
| Arsenic, ppb | 10 | 2000 |

TABLE III-38

CATALYST ANALYSIS - IN SITU SHALE OIL
HYDROTREATER CATALYST AGING
10/5/79 - 11/2/79

| <u>Pre-Heat Section of Tab Alumina</u> | <u>% C</u> | <u>% Fe</u> | <u>% As</u> |
|--|------------|-------------|-------------|
| Upper Bed | 3.26 | 0.16 | 0.06 |
| Middle Bed | 2.22 | 0.16 | 0.02 |
| Lower Bed | 1.31 | 0.05 | 0.04 |
| <u>Catalyst Bed</u> | | | |
| Top Section | 21.7 | 0.64 | 0.25 |
| Middle Section | 21.2 | 0.33 | 0.11 |
| Bottom Section | 23.7 | 0.21 | 0.06 |

DISCUSSION

This run successfully demonstrated the potential for a crude shale hydrotreater to be operated at relatively modest pressure while maintaining reasonable operating results. Of particular importance, maintenance of hydrogenation and stable denitrogenation activity was demonstrated. Actual desulfurization attained was somewhat disappointing and may be due to the product work-up procedure used.

SECTION IV

FLUID CATALYTIC CRACKING OF IN SITU SHALE OIL

A major key of the EXTRACTACRACKING process is fluid catalytic cracking (FCC) of high nitrogen feedstocks. Objectives for this module are to convert an economic maximum of gas oil and heavier material into jet fuel and gasoline boiling range products. Secondary objectives for the FCC module are reduction of heteroatom (sulfur, nitrogen, oxygen) content without hydrotreating, and selectively redistributing the available hydrogen already in the heavy shale fractions so that the distillate product exhibits a hydrogen content greater than the FCC feed, again without external addition of hydrogen.

Due to the short experimental time available, which required a priori definition of experimental conditions with little opportunity for feedback from other process modules, a wide range of conditions and experimentation was provided. Fluid catalytic cracking studies were provided in the following manner:

1. Microactivity tests - provide yield-response curves as a function of feedstock, hydrotreater severity and FCC severity.
2. FCC M-series tests - provide single condition source specific data, including detailed product

properties and material for further processing, as a function of hydrotreater catalyst and fractionator endpoint.

3. FCR Oxy tests - provide single condition source specific data, including detailed product properties and material for further processing as a function of hydrotreater catalyst age. Evaluate charging the entire crude shale hydrotreater to the FCC unit.
4. MAT recycle tests - provide yield-response data for selected recycle streams.

Test sets 1-3 are on a fresh-feed basis, while test set 4 evaluates options available on an independent recycle basis. Test sets 2 and 3 provide independent comparison of continuous versus MAT (batch) data, and allow some normalization and/or confirmation of the smaller scale data.

1. MAT TESTS-FRESH FEED

SUMMARY

A total of 50 catalytic cracking data points (yield structures) have been developed for hydrotreated 600°F+ in situ shale oil. Operating severities were varied, resulting in 33 to 95 weight percent conversions to <600°F material. Data were developed to demonstrate the impact of both basic nitrogen content and hydrotreater catalyst type. Cobalt and nickel molybdate catalysts provided equivalent

cracking yields, except for the higher severity region where nickel molybdate may be favored. Very surprising results were obtained when nitrogen extract was included in the FCC yields, in that the expected yield depression was not observed.

OBJECTIVES

Target objectives for these studies were to develop, in a rapid manner, FCC yield response parameters for crude shale hydrotreater products as a function of hydrotreater severity, boiling fraction, nitrogen content and FCC unit severity.

UNIT DESCRIPTION

These MAT small scale screening runs were being carried out in the 15mm I.D., 38cm length quartz reactor of a Micro Activity Test (MAT) Unit of the type used for some years by oil industry and catalyst manufacturer research laboratories. This "MAT" is not universally standardized, but one version has been recommended for acceptance as a standard by the ASTM D-32 committee on catalysts. The reactor is positioned vertically. A 2 to 8 gram charge of molecular sieve-containing (and/or amorphous) fluidized bed type cracking catalyst is held stationary in a constant temperature zone of an electrically heated furnace. Feedstock in the amount of 0.5 to 4 grams is delivered at constant rate downflow from a syringe. The feed oil is vaporized before contact with the catalyst. Vaporization is

accomplished by low voltage resistance heating of the 18 gauge stainless steel tubing of a deadman-preheater insert above the catalyst bed within the quartz reactor. Product synthetic crude liquid is condensed and where necessary weathered at the end of the on-stream period. Gas produced is collected and measured above brine solution in a calibrated Pyrex vessel.

EXPERIMENTAL

For each sample subjected to MAT analysis, a range of conditions comprising varying temperature, catalyst-to-oil ratio and/or WHSV were selected based on a priori estimation of conditions required to obtain 30-90 percent conversion. Each data point was evaluated and, where necessary, repeated. Additional runs were performed as needed to define the "knee" or maximum distillate liquid yield region.

For each run, the standard catalyst (equilibrium commercial FCC sample) was regenerated in a muffle furnace for 2 hours at 1100°F. The catalyst charge, actual weight depending on the WHSV of operation, was placed in the unit and purged of air. After equilibration at temperature, feed was injected and the unit nitrogen purged to a specified total nitrogen flow.

Product liquids were collected in tared liquid traps, and analyzed with a gravitometer and by simulated distillation (ASTM D-2887). Product gas was collected via calibrated brine displacement and analyzed by gas chromatography. Coke yield was measured by carbon content of the recovered catalyst.

Yield calculations and data reported were based on the specified feed cut point, after adjusting for the amount of material lighter than the specified cut point in the feed. The material lighter than the specified cut point is assumed to be unreactive.

FEEDSTOCK

A broad range of feedstocks was used for these tests. In particular, the evaluation sequence was to evaluate options available in the crude shale hydrotreater, including severity, catalyst and fractionation cut point. A further sample was prepared by doping with nitrogen extract to a very high basic nitrogen level, giving four increments of basic nitrogen feed.

The five digit figures refer to samples prepared during the previously reported (see Section III) parameter variation studies. Samples 11103, 11205 and 11312 were produced over cobalt molybdate catalyst, while 12205 was produced over nickel molybdate catalysts. The M-112 600°F+ hydrotreater product described in Section III, which had also been cracked on the FCR unit (Part 2 of this Section), was used to make sample DM 112 by blending this material

with extract from the nitrogen extraction section. This sample was processed to evaluate the feasibility of utilizing the by-product extract by blending it to the FCC unit. Since the M-112 sample was prepared using cobalt molybdate catalyst, this also provides an upper bound for the effect of nitrogen on FCC operations when charging cobalt molybdate hydrotreater products. Pertinent properties for each of these feedstocks are shown in Table IV-1.

RESULTS

Detailed results and graphical presentation of these data are shown in Tables IV-2 through IV-6 and Figures IV-1 through IV-12. For definition of terms, the reader should consult the list of abbreviations and terms.

DISCUSSION

A very large quantity of data was collected in these studies. Conversions ranging from 33.8 to 95.6 weight percent, based on a 600°F reference, were obtained for feedstocks ranging from 0.1 to 1.02 weight percent basic nitrogen. For modeling purposes, yield structures were determined over a range of conversions which included definition of the maximum distillate yield region.

A datum of particular interest is the dependence of conversion and yields on basic nitrogen content of comparable feedstocks. Selected data are plotted for the three cobalt molybdate based stocks in Figure IV-11. Even though a shortage of data exists in the moderate nitrogen region

TABLE IV-1

MICROACTIVITY TESTS **FRESH FEEDSTOCK**

| Sample | 11103 | 11205 | 11312 | DM112 | 12205 |
|----------------------------|--------|--------|---------|--------|--------|
| °API | 21.3 | 22.8 | 28.9 | 23.3 | 23.5 |
| Carbon | - | 87.3 | - | - | - |
| Hydrogen | - | 11.73 | - | - | - |
| Nitrogen | (1.42) | (1.29) | (0.213) | (1.60) | (1.16) |
| Basic Nitrogen | 0.95 | 0.86 | 0.10 | 1.02 | 0.85 |
| Sulfur | 0.31 | 0.13 | 0.05 | - | 0.08 |
| Simulated Distillation, °F | | | | | |
| IBP | 529 | 514 | 596 | 377 | 559 |
| 10 | 599 | 582 | 642 | 603 | 608 |
| 50 | 751 | 738 | 756 | 745 | 745 |
| 90 | 915 | 906 | 902 | 908 | 897 |
| EP | 982 | 978 | 963 | 989 | 957 |

All units are weight percent unless specified

TABLE IV-2

MILITARY JET FUEL FROM SHALE OIL PHASE II MAT SUMMARY

| RUN NO. | 20 | 22 | 25 | 28 | 54 | 55 | 57 |
|--|-------|------|-------|------|------|------|-------|
| <u>FEEDSTOCK</u> CONDITIONS | 11103 | | | | | | |
| TEMP., °F | 1000 | 1000 | 1050 | 950 | 1000 | 1050 | 950 |
| CAT./OIL | 12.0 | 5.6 | 5.8 | 6.4 | 2.9 | 3.1 | 3.0 |
| WHSV | 7.9 | 8.6 | 8.3 | 7.5 | 15.9 | 15.0 | 15.4 |
| TEST RESULTS | | | | | | | |
| RECOVERY, WTZ | 94.0 | 95.5 | 92.6 | 99.7 | 96.8 | 93.1 | 100.4 |
| CONV. OF 600°F ⁺ | 89.6 | 78.5 | 86.0 | 69.8 | 57.5 | 72.4 | 46.6 |
| TOTAL CONV., WTZ | | | | | | | |
| to C ₅ -400°F, WTZ | 27.8 | 31.3 | 13.1 | 27.0 | 20.7 | 26.9 | 17.7 |
| VOLZ | 33.7 | 37.9 | 37.6 | 32.7 | 25.0 | 32.5 | 21.4 |
| SELECTIVITY | 0.37 | 0.47 | 0.43 | 0.46 | 0.41 | 0.44 | 0.43 |
| to 400-600°F, WTZ | 5.6 | 13.6 | 8.8 | 13.2 | 14.8 | 16.9 | 15.0 |
| VOLZ | 6.2 | 14.9 | 9.6 | 14.5 | 16.3 | 18.5 | 16.5 |
| SELECTIVITY | 0.07 | 0.19 | 0.11 | 0.20 | 0.27 | 0.25 | 0.33 |
| to C ₄ MINUS GAS, WTZ | 37.9 | 22.7 | 32.9 | 20.8 | 18.2 | 23.9 | 10.9 |
| *(GAS, WTZ FEED) | 37.0 | 26.5 | 32.0 | 24.7 | 20.0 | 23.6 | 11.4 |
| *(GAS, WTZ RECOVERY) | 39.3 | 27.8 | 34.6 | 24.7 | 20.6 | 25.6 | 11.3 |
| to COKE, WTZ | 18.2 | 10.9 | 13.3 | 8.7 | 3.8 | 4.7 | 3.0 |
| (WTZ C on FEED) | 15.3 | 9.3 | 11.0 | 7.8 | 3.3 | 3.9 | 2.7 |
| (WTZ C on RECOVERY) | 16.3 | 9.8 | 11.9 | 7.8 | 3.4 | 4.2 | 2.7 |
| UNCONVERTED 600°F ⁺ , WTZ | 10.4 | 21.5 | 14.0 | 30.2 | 42.5 | 27.6 | 53.4 |
| UNCONVERTED 600°F ⁺ , VOLZ | 10.8 | 22.5 | 14.6 | 31.5 | 44.3 | 28.8 | 55.7 |
| PRODUCTS, WTZ RECOVERY | 99.9 | 100 | 100.1 | 99.9 | 100 | 100 | 100 |
| C ₅ - 600°F RECOVERED, VOLZ | 39.9 | 52.8 | 47.2 | 47.2 | 41.3 | 51.0 | 37.9 |

Note: Conversions Determined on a Recovered Weight Basis
* Total Gas, Includes C₅+ Components

TABLE IV-3
MILITARY JET FUEL FROM SHALE OIL
PHASE II MAT SUMMARY

| RUN NO. <u>ANALYST</u> <u>CONDITIONS</u> <u>TEMP., °F</u> <u>CAT./OIL</u> <u>WHSV</u> | 11208 | | | | | | | | | | | 36 |
|--|-------|-------|------|-------|------|-------|------|-------|------|------|------|------|
| | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 33 | 1050 | 1050 | 1000 | 1000 |
| TEST RESULTS | 900 | 100 | 1000 | 1050 | 950 | 1000 | 1050 | 1050 | 1050 | 1050 | 1000 | 1000 |
| RECOVERY, WT% | 3.0 | 3.0 | 3.0 | 2.9 | 6.1 | 6.5 | 6.2 | 10.3 | 6.2 | 6.2 | 12.0 | 12.0 |
| CONV. OF 600°F ⁺ | 15.8 | 15.8 | 15.5 | 15.9 | 7.9 | 6.9 | 7.7 | 9.2 | 7.7 | 7.7 | 7.9 | 7.9 |
| TOTAL CONV., WT% | 101.9 | 102.5 | 97.3 | 94.8 | 96.0 | 100.7 | 91.8 | 97.6 | 91.8 | 91.8 | 96.2 | 96.2 |
| to C ₅ -400°F, WT% | 33.8 | 46.8 | 55.8 | 78.3 | 67.4 | 81.8 | 84.0 | 89.6 | 84.0 | 84.0 | 86.0 | 86.0 |
| VOL% | 15.2 | 17.0 | 24.6 | 30.2 | 28.5 | 35.0 | 31.9 | 33.1 | 31.9 | 31.9 | 33.0 | 33.0 |
| SELECTIVITY | 18.3 | 20.4 | 29.5 | 36.2 | 34.2 | 42.0 | 38.3 | 39.7 | 38.3 | 38.3 | 39.6 | 39.6 |
| SELECTIVITY | 0.44 | 0.39 | 0.49 | 0.45 | 0.48 | 0.50 | 0.45 | 0.44 | 0.45 | 0.45 | 0.45 | 0.45 |
| to 400-600°F, WT% | 6.5 | 9.3 | 13.1 | 9.5 | 12.3 | 10.1 | 5.7 | 0.4 | 5.7 | 5.7 | 1.8 | 1.8 |
| VOL% | 7.0 | 10.1 | 14.2 | 10.3 | 13.4 | 11.0 | 6.2 | 0.4 | 6.2 | 6.2 | 1.9 | 1.9 |
| SELECTIVITY | 0.17 | 0.19 | 0.23 | 0.13 | 0.19 | 0.13 | 0.07 | < .01 | 0.07 | 0.07 | 0.02 | 0.02 |
| to C ₆ MINUS GAS, WT% | 8.8 | 16.7 | 14.6 | 31.7 | 18.5 | 26.0 | 33.3 | 42.1 | 33.3 | 33.3 | 35.1 | 35.1 |
| *(GAS, WT% FEED) | 13.1 | 18.4 | 18.5 | 33.2 | 21.6 | 31.8 | 35.4 | 47.2 | 35.4 | 35.4 | 37.9 | 37.9 |
| *(GAS, WT% RECOVERY) | 12.9 | 18.0 | 19.0 | 35.1 | 22.5 | 31.6 | 38.6 | 48.4 | 38.6 | 38.6 | 39.4 | 39.4 |
| to COKE, WT% | 3.3 | 3.7 | 3.5 | 7.0 | 8.0 | 10.7 | 13.1 | 14.1 | 13.1 | 13.1 | 16.0 | 16.0 |
| (WTZ C on FEED) | 2.9 | 3.3 | 2.9 | 5.6 | 6.6 | 9.3 | 10.3 | 11.8 | 10.3 | 10.3 | 13.3 | 13.3 |
| (WTZ C on RECOVERY) | 2.8 | 3.2 | 3.0 | 6.0 | 6.9 | 9.2 | 11.3 | 12.1 | 11.3 | 11.3 | 13.8 | 13.8 |
| UNCONVERTED 600°F ⁺ , WT% | 66.2 | 53.2 | 44.2 | 21.7 | 32.6 | 18.2 | 16.0 | 10.4 | 16.0 | 16.0 | 14.0 | 14.0 |
| UNCONVERTED 600°F ⁺ , VOL% | 68.4 | 55.0 | 45.7 | 22.4 | 33.7 | 18.8 | 16.5 | 10.8 | 16.5 | 16.5 | 14.5 | 14.5 |
| PRODUCTS, WT% RECOVERY | 100 | 99.9 | 100 | 100.1 | 99.9 | 100 | 100 | 100.1 | 99.9 | 100 | 99.9 | 99.9 |
| C ₅ - 600°F RECOVERED, VOL% | 25.3 | 30.5 | 42.7 | 46.5 | 47.6 | 53.0 | 44.5 | 40.1 | 44.5 | 44.5 | 41.5 | 41.5 |

Note: Conversions Determined on a Recovered Weight Basis
* Total Gas, Includes C₅ Components

TABLE IV-4
MILITARY JET FUEL FROM SHALE OIL
PHASE II MAT SUMMARY

| RUN NO. | 37 | 40 | 42 | 43 | 45 | 47 | 50 | 51 | 52 |
|--|-------|------|------|------|-------|------|------|------|------|
| <u>FEEDSTOCK</u> | 11312 | | | | | | | | |
| <u>CONDITIONS</u> | | | | | | | | | |
| TEMP., °F | 1000 | 1000 | 1050 | 1050 | 950 | 950 | 1050 | 1000 | 1000 |
| CAT./OIL | 11.6 | 5.8 | 7.0 | 6.9 | 6.4 | 3.6 | 3.3 | 3.1 | 3.1 |
| WHSV | 8.2 | 8.3 | 6.9 | 7.0 | 7.5 | 13.1 | 14.4 | 15.0 | 15.0 |
| <u>TEST RESULTS</u> | | | | | | | | | |
| RECOVERY, WT% | 97.9 | 91.8 | 95.1 | 85.3 | 98.2 | 98.0 | 99.7 | 97.5 | 91.4 |
| CONV. OF 600°F+ | 95.6 | 92.2 | 95.3 | 94.9 | 94.1 | 75.0 | 77.9 | 69.3 | 67.8 |
| TOTAL CONV., WT% | | | | | | | | | |
| to C ₅ -400°F, WT% | 38.2 | 45.9 | 38.8 | 42.3 | 55.5 | 41.3 | 37.1 | 36.5 | 33.3 |
| to C ₅ -400°F, VOL% | 44.1 | 52.9 | 44.8 | 48.8 | 63.9 | 47.7 | 42.8 | 42.0 | 38.4 |
| SELECTIVITY | 0.46 | 0.52 | 0.47 | 0.51 | 0.68 | 0.63 | 0.55 | 0.60 | 0.56 |
| to 400-600°F, WT% | 6.8 | 9.5 | 7.3 | 8.8 | 9.8 | 12.7 | 13.4 | 11.6 | 15.0 |
| to 400-600°F, VOL% | 7.1 | 9.9 | 7.6 | 9.2 | 10.2 | 13.3 | 14.1 | 12.1 | 15.7 |
| SELECTIVITY | 0.07 | 0.11 | 0.08 | 0.10 | 0.11 | 0.18 | 0.18 | 0.17 | 0.23 |
| to C ₄ MINUS GAS, WT% | 36.9 | 30.2 | 39.9 | 34.1 | 22.0 | 17.8 | 25.4 | 18.3 | 17.0 |
| * (GAS, WT% FEED) | 49.2 | 37.8 | 53.4 | 42.8 | 39.7 | 30.7 | 37.6 | 25.9 | 25.0 |
| * (GAS, WT% RECOVERY) | 50.3 | 41.2 | 56.1 | 50.2 | 40.5 | 31.3 | 37.7 | 26.6 | 27.3 |
| to COKE, WT% | 13.7 | 6.6 | 9.3 | 9.7 | 6.9 | 3.1 | 2.0 | 2.9 | 2.5 |
| (WT% C on FEED) | 13.2 | 6.0 | 8.7 | 8.2 | 6.7 | 3.1 | 2.0 | 2.8 | 2.3 |
| (WT% C on RECOVERY) | 13.5 | 6.5 | 9.2 | 9.6 | 6.8 | 3.1 | 2.0 | 2.9 | 2.5 |
| UNCONVERTED 600°F+, WT% | 4.4 | 7.8 | 4.7 | 5.1 | 5.9 | 25.0 | 22.1 | 30.7 | 32.2 |
| UNCONVERTED 600°F+, VOL% | 4.3 | 7.7 | 4.6 | 5.0 | 5.9 | 24.9 | 21.9 | 30.5 | 32.0 |
| <u>EPRODUCTS, WT% RECOVERY</u> | 100 | 100 | 100 | 100 | 100.1 | 99.9 | 100 | 100 | 100 |
| C ₅ - 600°F RECOVERED, VOL% | 51.2 | 62.8 | 52.4 | 58.0 | 74.1 | 61.0 | 56.9 | 54.1 | 54.1 |

Note: Conversions Determined on a Recovered Weight Basis
* Total Gas, Includes C₅ + Components

TABLE IV-5
MILITARY JET FUEL FROM SHALE OIL
PHASE II MAT SUMMARY

| RUN NO. | 68 | 69 | 70 | 71 | 72 | 73 | 74 | 75 | 80 | 81 | 82 | 83 | 88 | 89 |
|----------------------------------|--------------|------|-------|-------|------|------|------|------|------|------|-------|-------|------|-------|
| FEDERATION | M113 - 800 + | | | | | | | | | | | | | |
| CONDITIONS | | | | | | | | | | | | | | |
| TEMP., °F | 950 | 950 | 1000 | 1000 | 950 | 950 | 1000 | 1000 | 1000 | 1000 | 1050 | 1050 | 1050 | 1050 |
| CAT./OIL | 2.2 | 2.9 | 3.1 | 2.8 | 3.8 | 4.3 | 4.7 | 3.7 | 7.1 | 5.7 | 3.9 | 4.3 | 6.1 | 6.4 |
| WHSV | 21.3 | 16.0 | 15.2 | 16.5 | 13.1 | 11.7 | 10.6 | 13.6 | 7.0 | 8.5 | 12.8 | 12.4 | 7.9 | 7.5 |
| TEST RESULTS | | | | | | | | | | | | | | |
| RECOVERY, WT% | 92.5 | 93.2 | 96.0 | 92.7 | 99.1 | 94.3 | 90.8 | 92.4 | 94.1 | 97.8 | 91.8 | 92.8 | 92.1 | 89.4 |
| CONV. OF 600°F+ | 41.9 | 37.5 | 50.8 | 57.5 | 51.7 | 51.7 | 62.3 | 58.6 | 74.9 | 70.6 | 73.9 | 75.3 | 83.3 | 85.2 |
| TOTAL CONV., WT% | | | | | | | | | | | | | | |
| to C ₅ -400°F, WT% | 16.1 | 15.9 | 18.2 | 23.6 | 23.3 | 23.3 | 25.1 | 22.1 | 29.5 | 33.0 | 31.6 | 33.8 | 37.3 | 37.2 |
| VOL% | 19.2 | 19.0 | 21.7 | 28.2 | 27.8 | 27.6 | 29.9 | 26.4 | 35.2 | 39.5 | 37.7 | 40.4 | 44.5 | 44.5 |
| SELECTIVITY | 0.42 | 0.46 | 0.40 | 0.47 | 0.51 | 0.51 | 0.46 | 0.43 | 0.46 | 0.55 | 0.50 | 0.53 | 0.53 | 0.52 |
| to 400-600°F, WT% | 11.6 | 10.3 | 14.5 | 16.0 | 13.9 | 13.5 | 16.5 | 13.3 | 15.0 | 14.6 | 16.9 | 15.5 | 12.4 | 13.8 |
| VOL% | 12.5 | 11.1 | 15.7 | 17.3 | 15.0 | 14.6 | 17.9 | 14.4 | 16.3 | 15.8 | 18.3 | 16.8 | 13.5 | 14.9 |
| SELECTIVITY | 0.28 | 0.27 | 0.29 | 0.29 | 0.28 | 0.27 | 0.28 | 0.24 | 0.21 | 0.22 | 0.24 | 0.22 | 0.16 | 0.17 |
| to C ₆ MINUS GAS, WT% | 10.9 | 9.2 | 12.5 | 15.5 | 11.7 | 11.3 | 14.1 | 14.4 | 23.6 | 15.7 | 19.8 | 19.1 | 24.5 | 23.7 |
| (GAS, WT% FEED) | 12.7 | 8.9 | 13.3 | 17.6 | 16.7 | 14.1 | 15.6 | 13.6 | 26.9 | 25.2 | 21.8 | 24.9 | 28.5 | 21.5 |
| (GAS, WT% RECOVERY) | 13.8 | 9.5 | 13.9 | 19.0 | 16.9 | 15.0 | 17.2 | 16.8 | 28.6 | 25.8 | 23.8 | 26.8 | 30.9 | 24.0 |
| to COKE, WT% | 3.3 | 2.1 | 5.7 | 2.5 | 2.8 | 3.7 | 6.6 | 8.8 | 6.8 | 7.1 | 5.7 | 6.9 | 9.1 | 10.6 |
| (WT% C on FEED) | 2.8 | 1.8 | 5.0 | 2.1 | 2.6 | 3.3 | 5.4 | 7.4 | 5.8 | 6.4 | 4.8 | 5.8 | 7.7 | 8.6 |
| (WT% C on RECOVERY) | 3.0 | 1.9 | 5.2 | 2.3 | 2.6 | 3.4 | 6.0 | 8.0 | 6.2 | 6.5 | 5.2 | 6.3 | 8.3 | 9.7 |
| UNCONVERTED 600°F+, WT% | 58.1 | 62.5 | 49.2 | 42.5 | 48.3 | 48.3 | 37.7 | 41.4 | 25.1 | 29.4 | 26.1 | 24.7 | 16.7 | 14.8 |
| UNCONVERTED 600°F+, VOL% | 59.8 | 64.3 | 50.6 | 43.7 | 49.8 | 49.7 | 38.8 | 42.7 | 25.9 | 30.3 | 26.9 | 25.4 | 17.2 | 15.3 |
| | 100 | 100 | 100.1 | 100.1 | 100 | 99.9 | 100 | 100 | 100 | 99.8 | 100.1 | 100.1 | 100 | 100.1 |
| PRODUCTS, WT% RECOVERY | 37.1 | 30.1 | 37.4 | 45.5 | 42.8 | 42.2 | 47.8 | 40.8 | 51.5 | 55.3 | 56 | 57.2 | 58.0 | 59.4 |

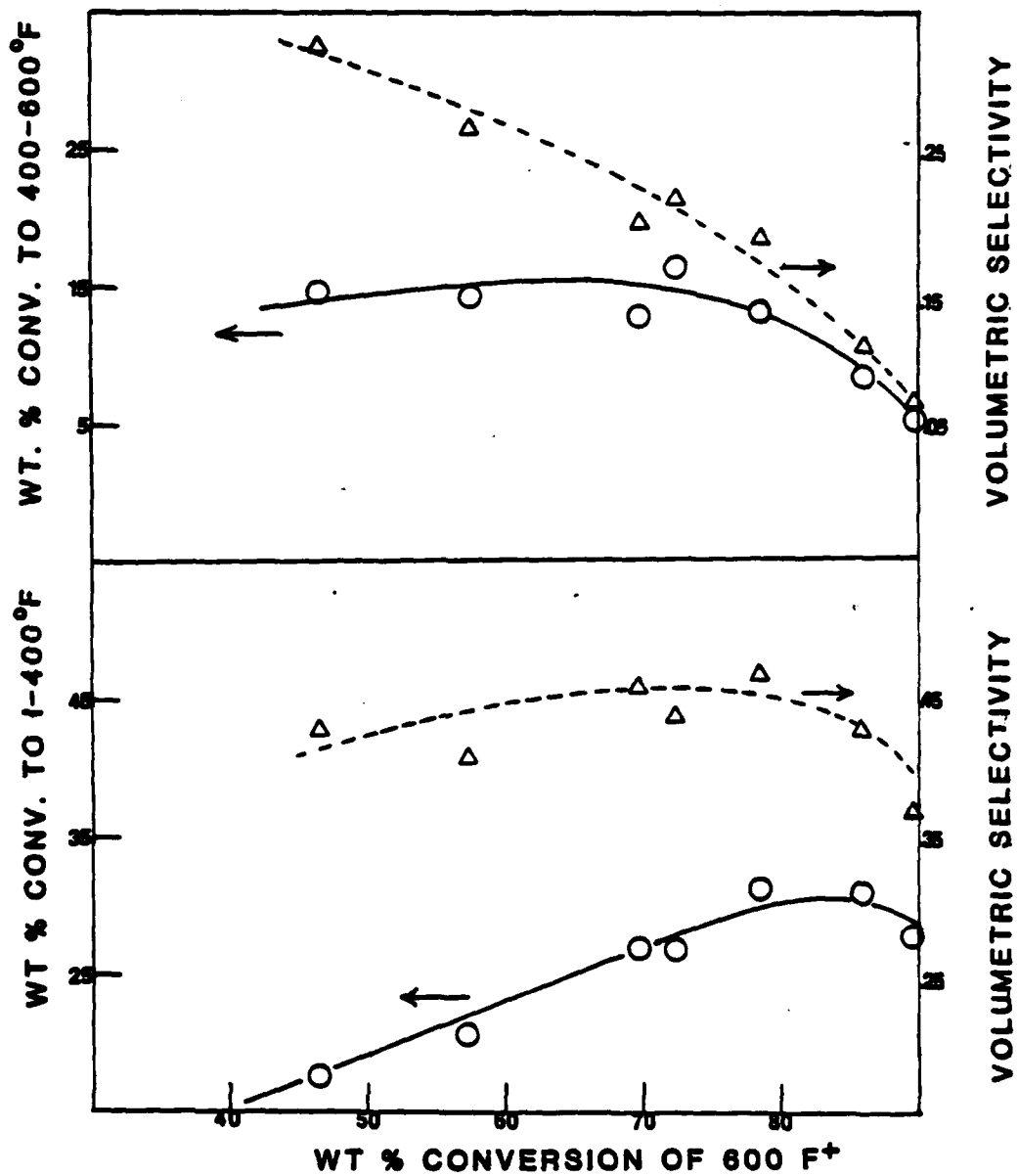
Note: Conversions Determined on a Recovered Weight Basis
* Total Gas, Includes C₅ + Components

TABLE IV-6

MILITARY JET FUEL FROM SHALE OIL PHASE II MAT SUMMARY

| RUN NO. | 59 | 60 | 61 | 62 | 63 | 64 | 67 | 76 | 77 | 78 | 79 |
|--|-------|-------|-------|------|------|------|------|-------|-------|------|------|
| <u>FEEDSTOCK</u> | 12205 | | | | | | | | | | |
| <u>CONDITIONS</u> | | | | | | | | | | | |
| TEMP., °F | 975 | 975 | 1050 | 1050 | 975 | 975 | 900 | 1000 | 1000 | 950 | 950 |
| CAT./OIL | 5.9 | 5.3 | 6.1 | 6.9 | 5.9 | 6.0 | 5.9 | 5.0 | 4.6 | 3.3 | 4.4 |
| WHSV | 8.2 | 9.1 | 7.9 | 7.0 | 8.2 | 8.0 | 8.1 | 10.8 | 10.8 | 14.4 | 10.6 |
| <u>TEST RESULTS</u> | | | | | | | | | | | |
| RECOVERY, WTZ | 94.6 | 92.1 | 87.0 | 89.5 | 90.4 | 94.5 | 96.9 | 97.6 | 93.2 | 92.9 | 92.4 |
| CONV. OF 600°F ⁺ | 75.9 | 69.6 | 84.2 | 89.5 | 75.2 | 70.0 | 50.7 | 66.3 | 66.2 | 41.9 | 49.6 |
| TOTAL CONV., WTZ | | | | | | | | | | | |
| to C ₅ -400°F, WTZ | 35.5 | 32.0 | 31.5 | 29.5 | 29.3 | 32.6 | 22.0 | 30.3 | 28.7 | 17.7 | 17.5 |
| VOLZ | 42.3 | 38.2 | 37.5 | 35.3 | 35.0 | 38.9 | 26.3 | 36.2 | 34.2 | 21.1 | 19.2 |
| SELECTIVITY | 0.55 | 0.54 | 0.44 | 0.39 | 0.46 | 0.54 | 0.49 | 0.53 | 0.50 | 0.47 | 0.37 |
| to 400-600°F, WTZ | 15.2 | 16.3 | 11.8 | 7.9 | 15.5 | 14.6 | 11.0 | 12.7 | 15.4 | 11.4 | 13.4 |
| VOLZ | 16.4 | 17.6 | 12.7 | 8.6 | 16.8 | 15.8 | 11.9 | 13.7 | 16.7 | 12.3 | 14.5 |
| SELECTIVITY | 0.21 | 0.25 | 0.15 | 0.10 | 0.22 | 0.22 | 0.22 | 0.20 | 0.25 | 0.27 | 0.28 |
| to C ₆ MINUS GAS, WTZ | 18.1 | 15.9 | 33.7 | 43.4 | 23.2 | 18.0 | 12.8 | 16.7 | 15.4 | 9.0 | 13.7 |
| * (GAS, WTZ FEED) | 23.3 | 18.2 | 33.7 | 40.5 | 24.3 | 23.9 | 16.4 | 23.0 | 19.5 | 9.9 | 13.4 |
| * (GAS, WTZ RECOVERY) | 24.7 | 19.8 | 38.7 | 45.2 | 26.9 | 25.3 | 16.9 | 23.5 | 20.9 | 10.7 | 14.5 |
| to COKE, WTZ | 7.2 | 5.5 | 7.3 | 8.6 | 7.1 | 5.5 | 4.9 | 6.7 | 6.8 | 3.8 | 5.0 |
| (WTZ C on FEED) | 6.2 | 4.6 | 5.8 | 7.1 | 5.9 | 4.8 | 4.3 | 5.9 | 5.8 | 3.3 | 4.2 |
| (WTZ C on RECOVERY) | 6.6 | 5.0 | 6.7 | 7.9 | 6.5 | 5.0 | 4.5 | 6.1 | 6.2 | 3.5 | 4.6 |
| UNCONVERTED 600°F ⁺ , WTZ | 24.1 | 30.4 | 15.8 | 10.5 | 24.8 | 30.0 | 49.3 | 33.7 | 33.8 | 58.1 | 50.4 |
| UNCONVERTED 600°F ⁺ , VOLZ | 24.8 | 31.2 | 16.2 | 10.8 | 25.5 | 29.2 | 50.7 | 34.6 | 34.8 | 59.7 | 51.8 |
| PRODUCTS, WTZ RECOVERY | 100.1 | 100.1 | 100.1 | 99.9 | 99.9 | 99.9 | 100 | 100.1 | 100.1 | 100 | 100 |
| C ₅ - 600°F RECOVERED, VOLZ | 58.7 | 55.8 | 50.2 | 43.9 | 51.8 | 54.7 | 38.2 | 49.9 | 50.9 | 33.4 | 33.7 |

Note: Conversions Determined on a Recovered Weight Bases
* Total Gas, Includes C₅ + Components



**Figure IV-1. Microactivity Test Cracking
Sample 11103**

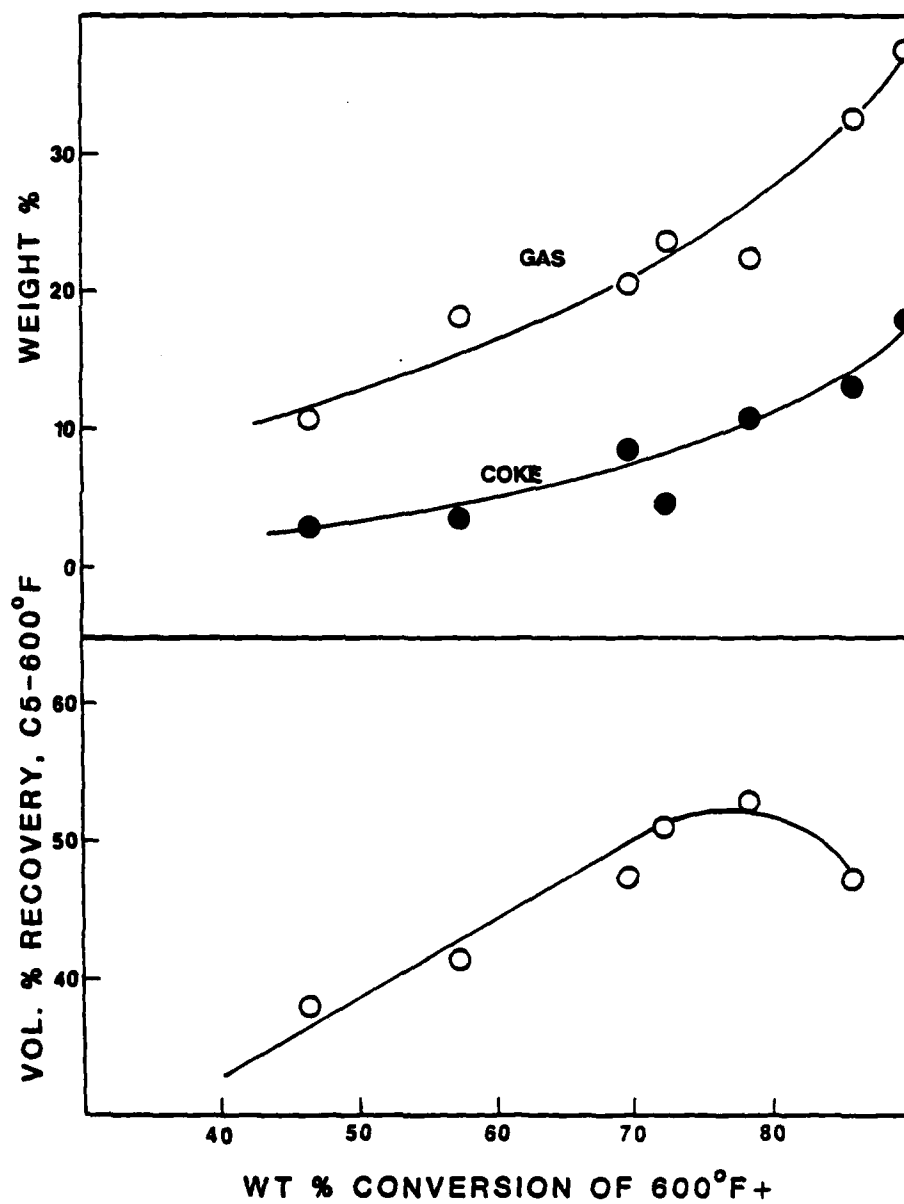
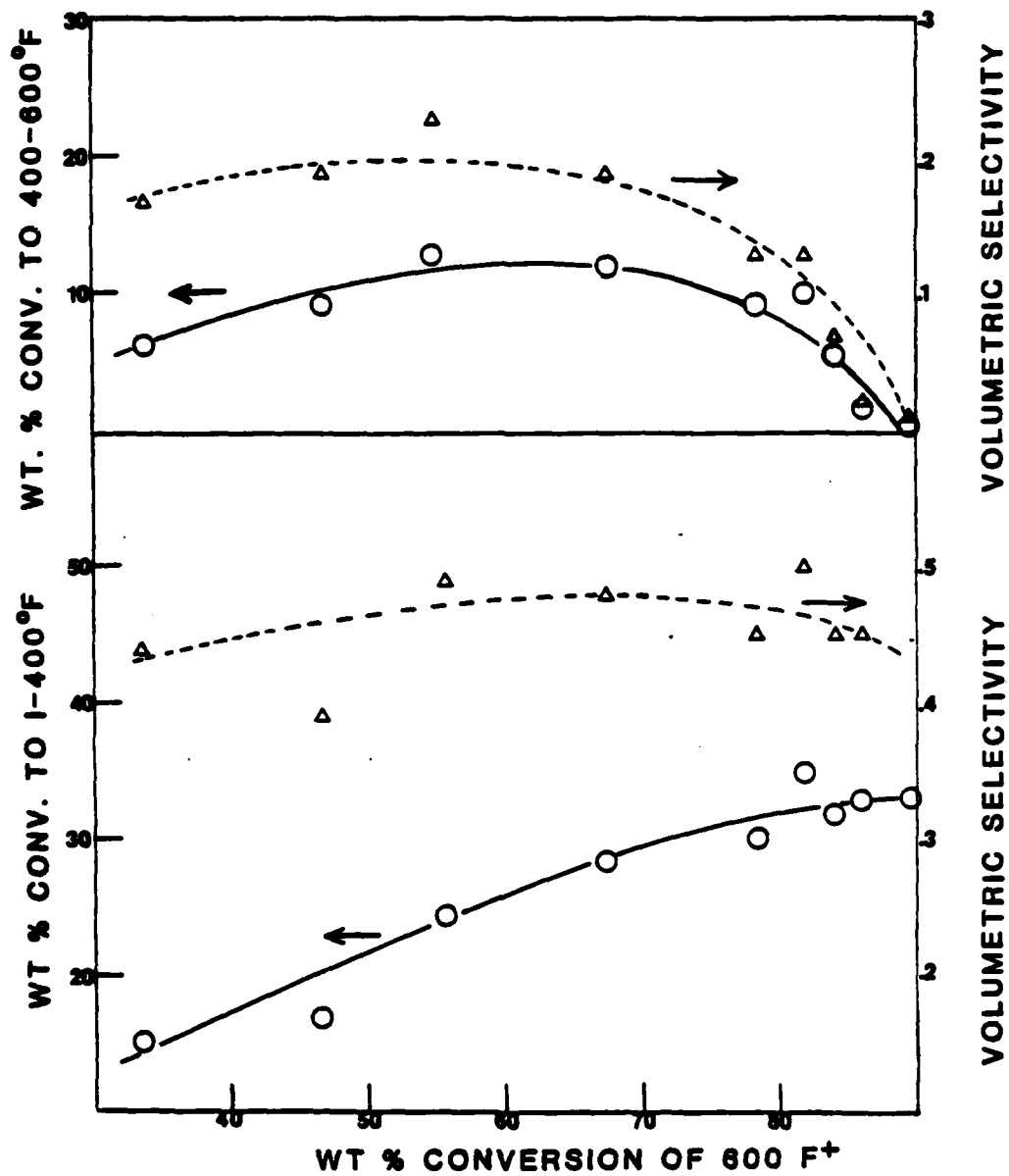


Figure IV-2. Microactivity Test Cracking
Sample 11103



**Figure IV-3. Microactivity Test Cracking
Sample 11205**

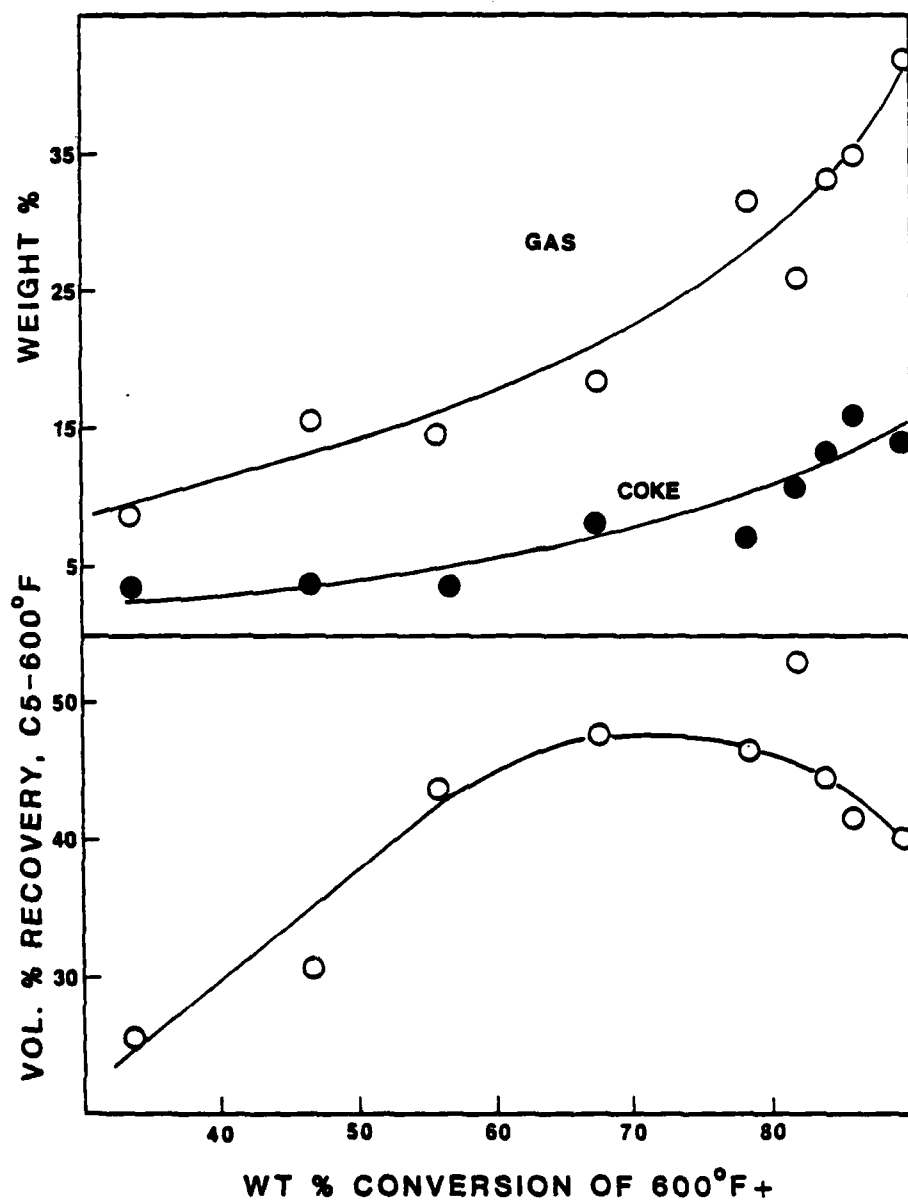
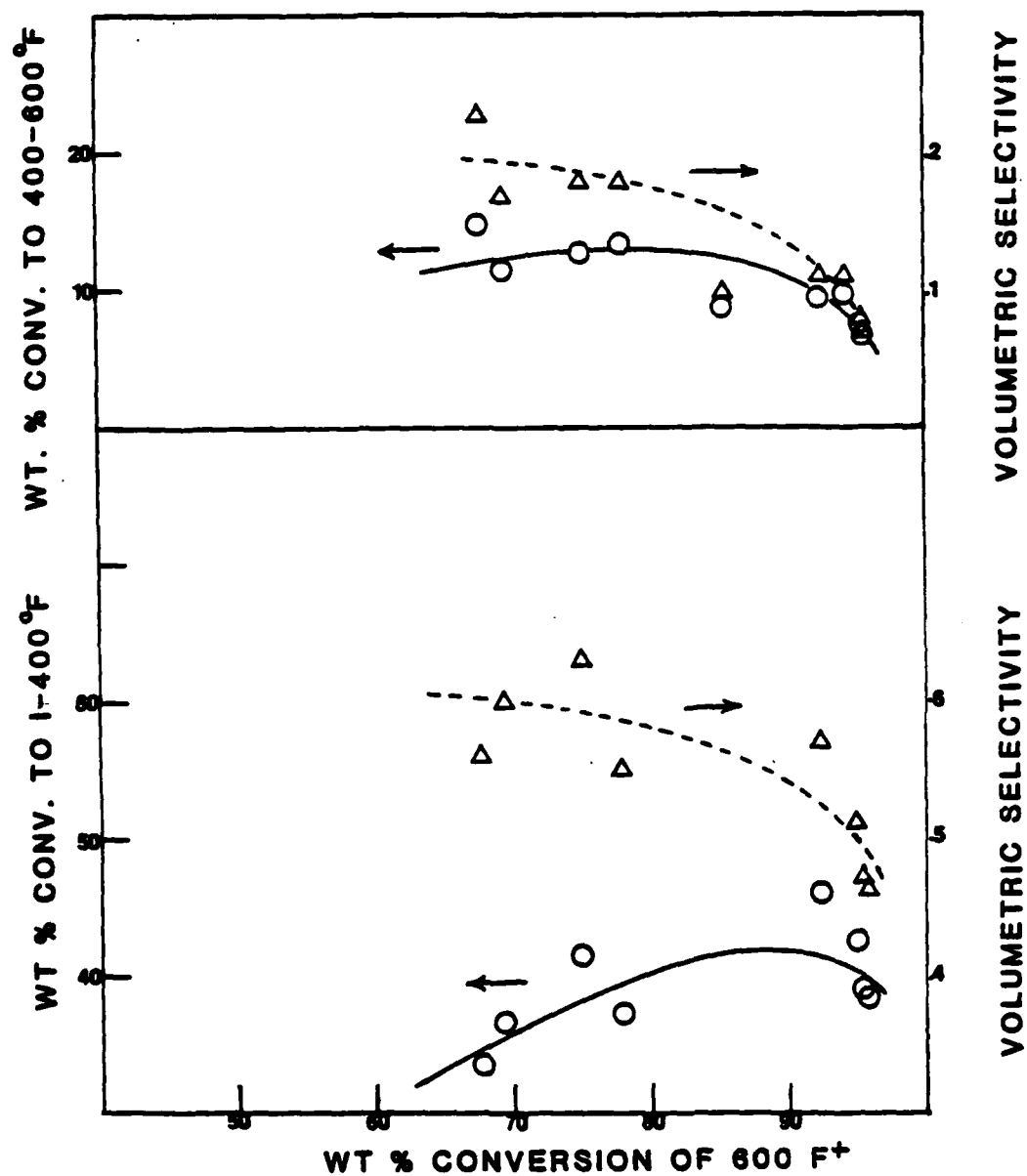


Figure IV-4. Microactivity Test Cracking
Sample 11205



**Figure IV-5. Microactivity Test Cracking
Sample 11312**

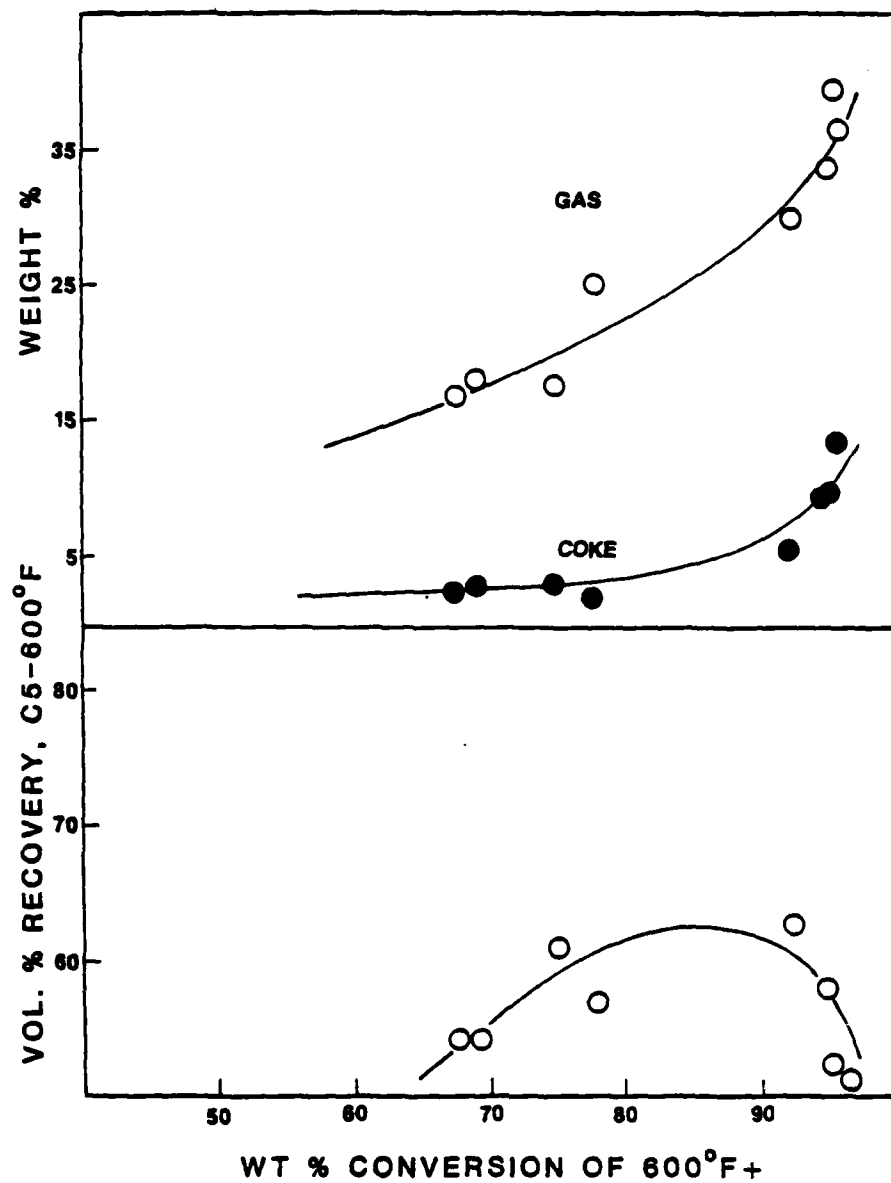


Figure IV-6. Microactivity Test Cracking
Sample 11312

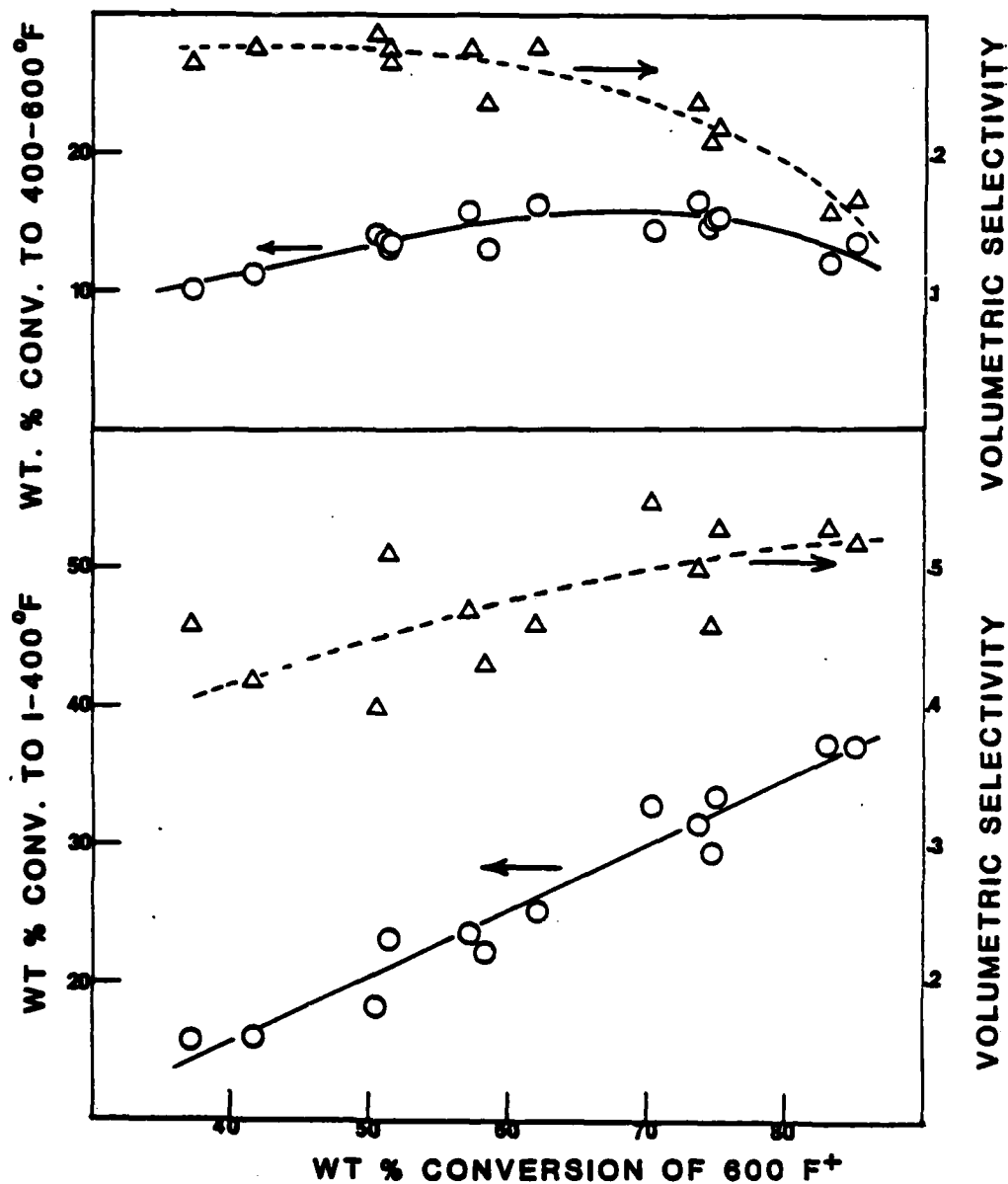


Figure IV-7. Microactivity Test Cracking
Sample M-112 600+

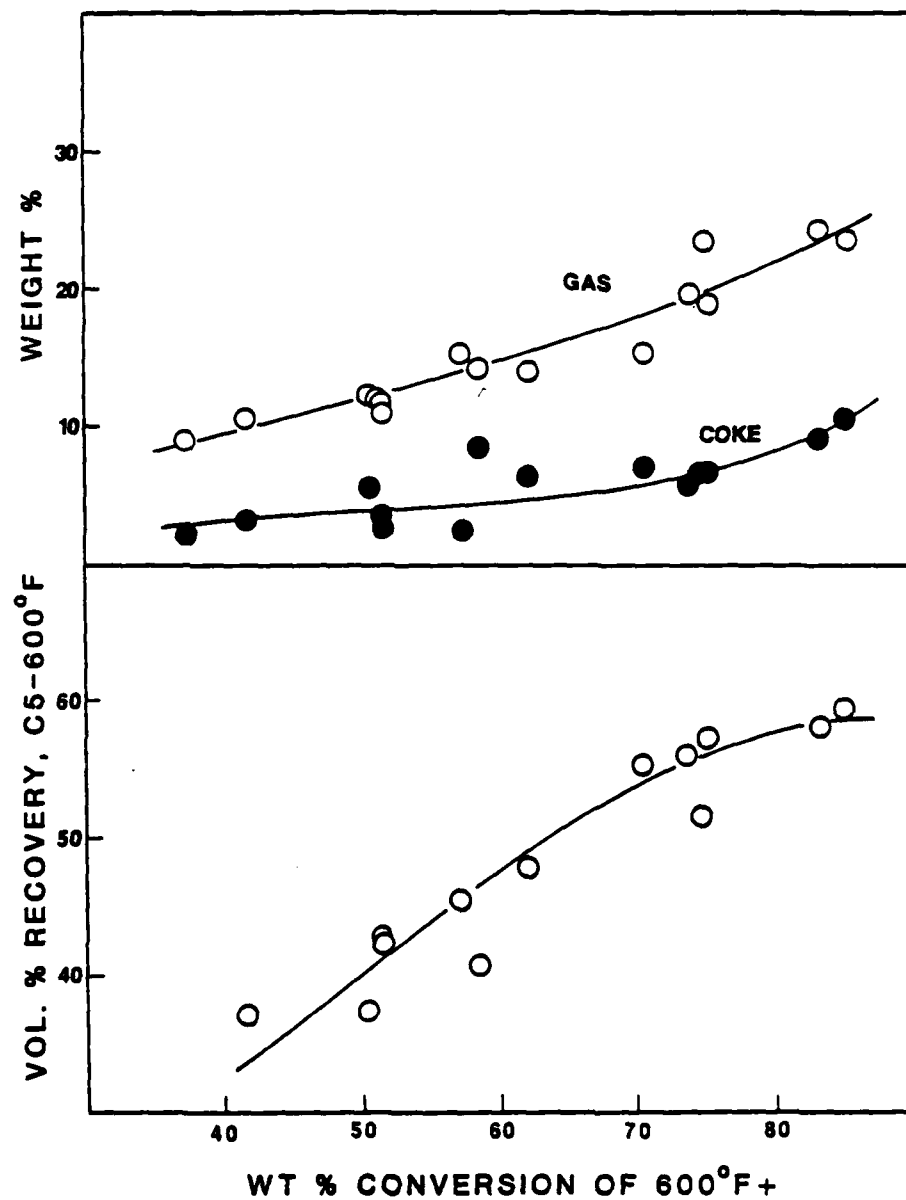


Figure IV-8. Microactivity Test Cracking
Sample M-112 600+

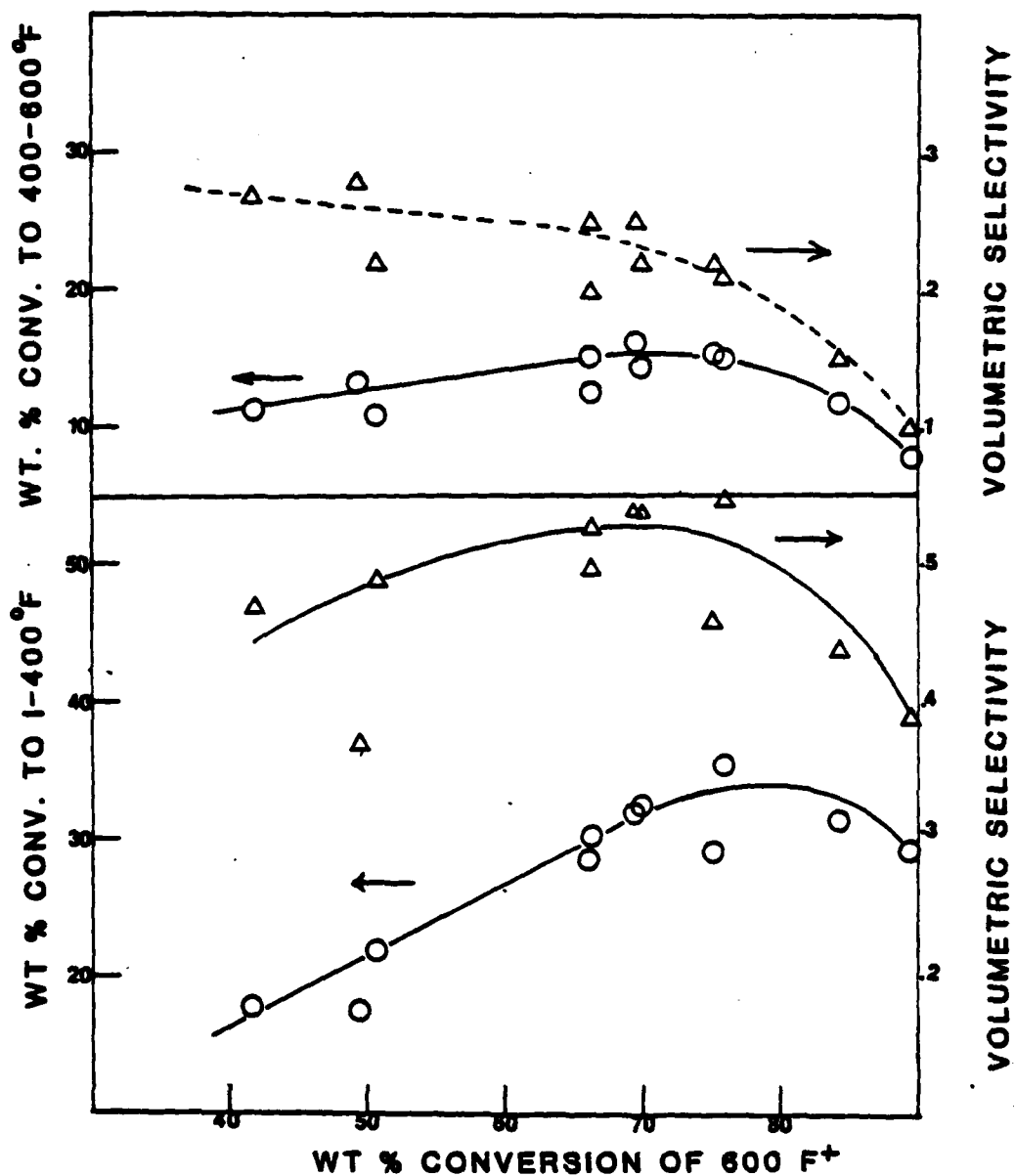


Figure IV-9. Microactivity Test Cracking
Sample 12205

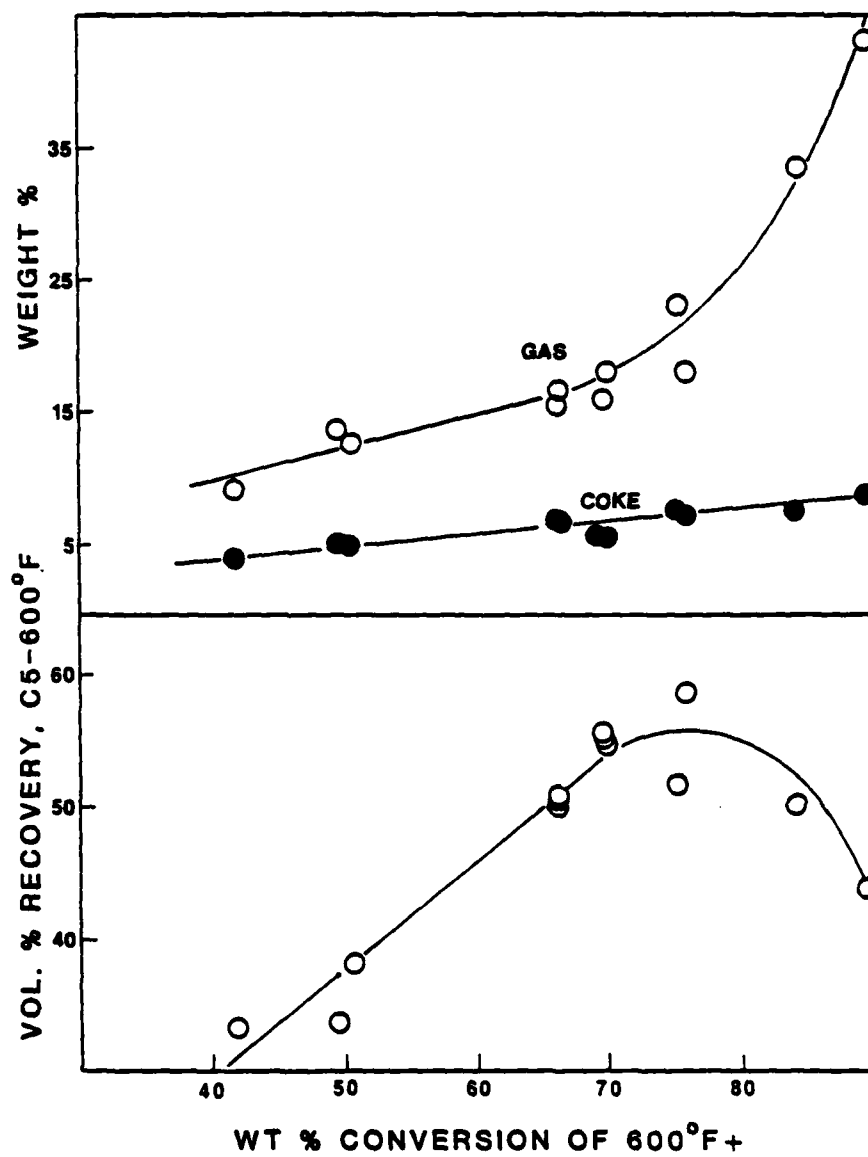


Figure IV-10. Microactivity Test Cracking
Sample 12205

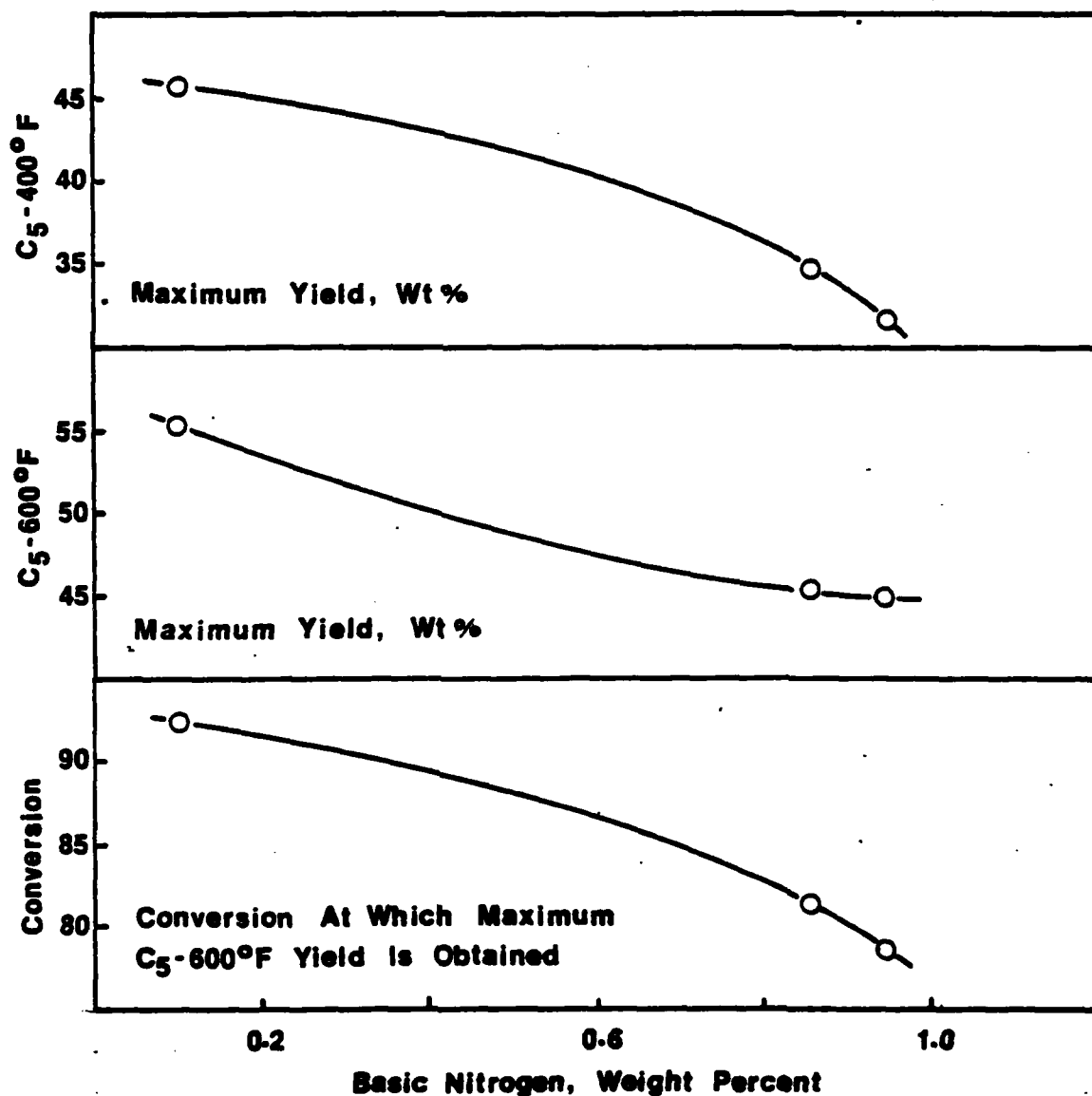


Figure IV-11. FCC Yield Maxima Dependence On Feedstock Basic Nitrogen Content For In Situ Shale Oil

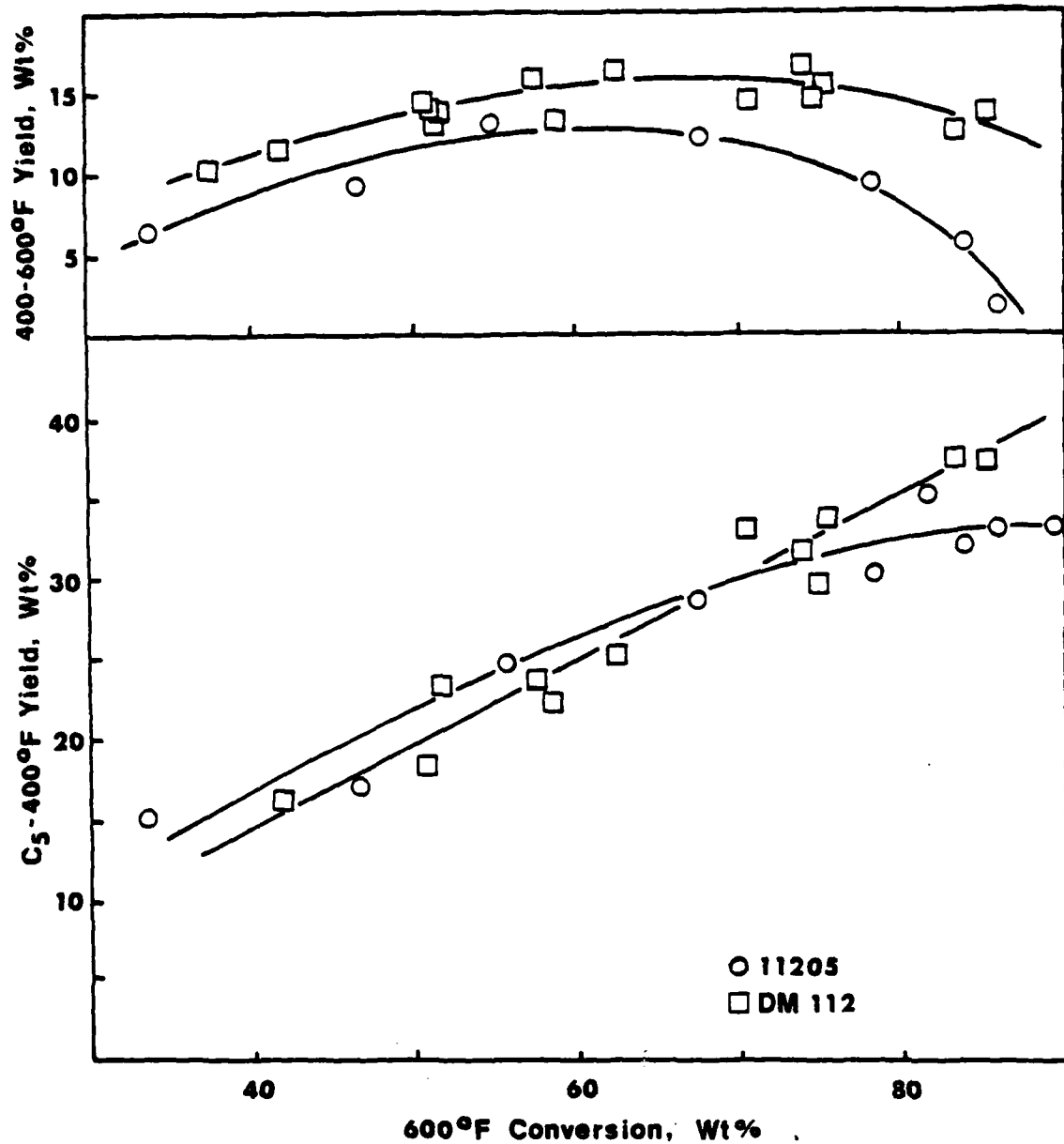


Figure IV-12. Comparison Of Nitrogen Doped
And The Analogous Fresh Feed Yields

(0.4-0.7), the correlation between yields and basic nitrogen content is very good. However, the change to different catalyst, as well as different nitrogen types (DM 112), does not follow this apparent correlation.

The data for the doped (DM 112) sample are somewhat surprising, as shown in Figure IV-12. These initial experiments were allocated to examine the potential for recovery of the nitrogen extract as a high value product by processing through the FCC unit, even though some yield depression was expected. As shown in the graphical analysis, this was not encountered, and in fact, the experimental yields obtained for the doped sample were superior to those obtained for the analogous (although not the same) fresh feed sample. These results are not immediately amenable to explanation, and further work should definitely be allocated to this aspect during Phase III. If, in fact, the same or improved yields are obtained when blending the nitrogen extract to cracker charge, the process itself will provide significantly improved economics.

Of further interest, a comparison of crude shale hydrotreater catalyst type as impacting the FCC fresh feed response shows apparently no significant difference in C₅-400°F yields between the two catalysts at analogous operating conditions in the crude shale hydrotreater. Other yield structures appear very similar as well, with the exception that the nickel molybdate based material may produce slightly lower gas yields at equivalent conversion

levels, and a possible higher maximum total distillate production. The primary difference appears to be that the nickel molybdate sample maintains an increasing distillate yield to higher levels of total conversion than the cobalt molybdate sample. These differences are relatively small, and may not actually portray levels of significant difference.

RECOMMENDATIONS AND CONCLUSIONS

- Higher hydrotreating severity provides better catalytic cracking yields and yield structure as expected.
- Conversions up to 95 weight percent (600°F basis) were obtained.
- Basic nitrogen content is a good correlative parameter for FCC yields only when the sample source parameters are constant.
- Crude shale hydrotreating over nickel molybdate catalyst may provide some yield selectivity advantage over cobalt molybdate catalyst, but only at the highest conversions evaluated.
- Feedstock doped with nitrogen extract demonstrated, on a consistent basis, equivalent or enhanced FCC performance when compared to the analogous undoped fresh feed chargestock.

2. FCR PROCESSING - M-SERIES (FRESH FEED)

SUMMARY

A circulating fluidized bed catalytic cracking unit was utilized in the pilot plant to catalytically crack, under specified conditions, nominal five gallon samples of varying quality shale oil feedstock. Full product yields and quality parameters were measured and adequate quantities of product collected for further processing. Successful processing on an integrated fluid cracking unit was demonstrated.

OBJECTIVES

Objectives for these studies were to: (1) demonstrate the validity of concurrently developed microactivity test data, (2) produce adequate quantities of material for further processing and (3) determine detailed product quality characteristics for varying feedstocks.

UNIT DESCRIPTION

The R&D fluid catalytic reactor (FCR) is a miniature version of full-scale operating FCC units. Specific details of the unit are proprietary, but in general, the unit is composed of a riser, a catalyst disengaging and stripping section, a regenerator and a regenerated catalyst standpipe. Regenerated catalyst is metered to the riser where it is admixed with oil feed by means of a slide valve. The catalyst/oil mixture flows in dilute phase to the catalyst disengaging section where the catalyst and

product vapors are separated, effectively terminating the reaction. Residual oil content is minimized in the stripping section and the stripped catalyst returned to the regenerator. Carbon content of the spent, stripped catalyst is removed by air combustion in the regenerator and the catalyst returned to the regenerated catalyst standpipe for reuse.

Catalyst inventory and circulation rates are such that the unit can be operated over varying time periods. The unit, due to its small size, is not heat balanced, being provided with external electrical resistance heaters on automatic temperature control. Product vapors are condensed and collected with product fractionation off line. All flows are measured to provide material balance capabilities and control for the system. Regenerator flue gas composition, spent catalyst carbon content and regenerated catalyst content are monitored for material balance purposes as well.

The unit has been developed over an extensive number of petroleum feedstocks and has been demonstrated to produce results correlatable to those obtained in commercial operations.

FEEDSTOCK

Two in situ source feedstocks were used in this study. Sample M-112 was produced in crude shale hydrotreater run M-112 over cobalt molybdate catalyst. The hydrotreater effluent was fractionated + 600°F and the +600°F product fed

to the FCR unit. Sample M-121 was produced in an analogous manner, with the exception of the use of nickel molybdate catalyst in the crude shale hydrotreater. Properties of each feedstock are shown in the results table for the appropriate sample.

EXPERIMENTAL

One charge of equilibrium zeolite FCC catalyst, obtained from Ashland's petroleum refining operations, was used for both M-112 and M-121 evaluations. Two three-hour material balance periods for each sample were performed.

Operations went smoothly in both cases and good material balance closures were obtained. During each run, product gas samples, regenerator flue gas samples, spent and regenerated catalyst samples and composite liquid product samples were collected and analyzed.

The remaining composite liquid samples were collected in five-gallon cans, batch fractionated and analyzed. The distillate product portion was supplied for further processing by extraction and the heavy liquid product retained for further upgrading studies.

RESULTS

Tables IV-7 and IV-8 summarize results for these samples. Conversions reported are based on actual +600°F feed and product yields obtained, while reported yields are as obtained without correction for -600°F material in the feed.

TABLE IV-7

**FLUID CATALYTIC CRACKING
FCR PROCESSING-SAMPLE M-12**

| Operating Conditions | | Liquid Properties | | | | |
|-------------------------------|------|---------------------------------------|--------|---------------|---------|---------|
| | | Item | Feed | Total Product | - 600°F | + 600°F |
| Temperature, °F | 970 | °API | 22.4 | 29.5 | 38.5 | 23.4 |
| Cat/Oil Ratio | 15.9 | Carbon, % _w | 86.9 | - | - | - |
| C on Regen Cat, % | 0.45 | Hydrogen, % _w | 11.7 | - | - | - |
| Conversion, Wt % ^a | 57.2 | Nitrogen, % _w | (1.09) | (0.731) | - | - |
| Closure, Wt % | 99.1 | N _{basic} , % _w | 0.816 | - | - | - |
| | | Sulfur, % _w | 0.17 | 0.10 | - | - |
| | | Oxygen, % _w | - | 0.176 | (0.174) | 0.178 |
| | | Rams C, % _w | 1.34 | - | - | - |
| | | Aromatics, % _w | - | - | - | - |
| | | GHV, Btu/lb | 18,977 | - | - | - |
| | | Distillation, Wt % (°F) by D2887 - 73 | | | | |
| | | IBP | - | 148 | - | - |
| | | 2 | 591 | 188 | - | - |
| | | 10 | 619 | 285 | - | - |
| | | 30 | 689 | 494 | - | - |
| | | 50 | 755 | 628 | - | - |
| | | 70 | 822 | 706 | - | - |
| | | 90 | 913 | 822 | - | - |
| | | 98 | 963 | 904 | - | - |
| | | EP | 980 | 935 | - | - |
| Product Yields, Wt % | | H ₂ | 0.22 | | | |
| | | C ₁ | 0.72 | | | |
| | | C ₂ | 1.96 | | | |
| | | C ₃ | 0.87 | | | |
| | | C ₃ ⁼ | 2.15 | | | |
| | | iC ₄ | 0.53 | | | |
| | | nC ₄ | 0.37 | | | |
| | | C ₄ ⁼ | 2.78 | | | |
| | | C ₅ - 600 | 34.91 | | | |
| | | 600 + | 43.1 | | | |
| | | Coke | 12.39 | | | |

^a - Based on the specified cut point above

() - Calculated

TABLE IV-8
FLUID CATALYTIC CRACKING
FOR PROCESSING-SAMPLE M-121

| Operating Conditions | | Liquid Properties | | | | |
|-------------------------------|-------|-------------------------------------|--------|---------------|---------|---------|
| | | Item | Feed | Total Product | - 600°F | + 600°F |
| Temperature, °F | 975 | °API | 22.9 | 31.7 | 42.5 | 22.5 |
| Cat/Oil Ratio | 14.7 | Carbon, % _w | 87.4 | - | - | - |
| C on Regen Cat, % | 0.02 | Hydrogen, % _w | 11.3 | - | - | - |
| Conversion, Wt % ^a | 64.7 | Nitrogen, % _w | (1.02) | (0.757) | (0.574) | (0.933) |
| Closure, Wt % | 98.0 | N _{basic} , % _w | 0.74 | - | - | - |
| | | Sulfur, % _w | 0.14 | 0.06 | - | 0.12 |
| | | Oxygen, % _w | - | 0.163 | (0.106) | 0.218 |
| | | Rams C, % _w | 1.53 | - | - | 0.98 |
| | | Aromatics, % _w | - | - | - | - |
| | | GHV, Btu/lb | 18,938 | - | - | - |
| Product Yields, Wt % | | Distillation, Wt % (°F) by D2887-73 | | | | |
| | | IBP | - | 96 | - | 530 |
| | | 2 | - | 145 | - | 548 |
| | | 10 | - | 238 | - | 603 |
| | | 30 | - | 411 | - | 652 |
| | | 50 | - | 605 | - | 702 |
| | | 70 | - | 690 | - | 766 |
| | | 90 | - | 814 | - | 853 |
| | | 98 | - | 916 | - | 921 |
| | | EP | - | 940 | - | 939 |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| H ₂ | 0.15 | | | | | |
| C ₁ | 0.0 | | | | | |
| C ₂ | 1.60 | | | | | |
| C ₃ | 0.64 | | | | | |
| C ₃ ⁼ | 2.81 | | | | | |
| iC ₄ | 0.73 | | | | | |
| nC ₄ | 0.31 | | | | | |
| C ₄ ⁼ | 4.01 | | | | | |
| C ₅ - 600 | 39.01 | | | | | |
| 600+ | 35.64 | | | | | |
| Coke | 15.10 | | | | | |

^a - Based on the specified cut point above
() - Calculated

DISCUSSION

Mechanical limitations presented two major difficulties during these runs. Both M-112 and M-121 required relatively high catalyst-to-oil ratios due to the small quantities of feed available. These excessive ratios led to relatively high coke yields, as demonstrated by the respective 12.4 and 15.1 weight percent coke yields for M-112 and M-121. Further, air flow limitations during processing of M-112 led to a high residual carbon level on regenerated catalyst, which biases the yield distribution and exacerbates the higher coke yield problem caused by high catalyst-to-oil ratios.

In spite of these problems, relatively good conversions (57-64 weight percent, 600°F basis) were obtained for both materials. These results are even slightly higher than the original (estimated) targeted conversion. As demonstrated in Tables IV-7 and IV-8, some heteroatom removal was accomplished, as well as hydrogen redistribution, in addition to the boiling-range conversion objectives.

RECOMMENDATIONS AND CONCLUSIONS

- Higher than desired catalyst-to-oil ratios, in both cases, and regenerated catalyst carbon level, for M-112, were encountered.
- Slightly higher conversions were attained than expected.

- Heteroatom removal and hydrogen redistribution were attained.
- Adequate products for further processing were collected.
- Detailed product qualities were developed.

3. FCR PROCESSING - OXY SAMPLE (FRESH FEED)

SUMMARY

A circulating fluidized bed catalytic cracking unit was utilized in the pilot plant to catalytically crack, under specified conditions, nominal five gallon samples of various qualities of shale oil feedstock. Full product yields and quality parameters were measured and adequate quantities of product collected for further processing. Successful processing on an integrated fluid cracking unit was demonstrated.

OBJECTIVES

Objectives for these studies were to: (1) demonstrate the validity of concurrently developed microactivity test data, (2) produce adequate quantities of material for further processing and (3) determine detailed product quality characteristics. These objectives are analogous to those delineated in Part 2 for the M-Series samples. Further objectives for these samples, however, were provided to: (1) evaluate the effect of feeding full-range crude shale hydrotreater product and (2) examine a series of samples

from the hydrotreater aging studies to determine the impacts of hydrotreater catalyst age on fluid cracking results.

EXPERIMENTAL

Experimental procedures for each of these runs were analogous to those utilized during the M-Series studies (Part 2). These runs were again relatively smooth, with reasonable material balance closures obtained in each case. Material balance periods ranged 4 to 5 hours each.

Sampling was also practiced in a manner analogous to the FCR M-Series runs. Each product composite was again fractionated $\pm 600^{\circ}\text{F}$, evaluated and utilized for further processing.

UNIT DESCRIPTION

The equipment and catalyst utilized are analogous to that described in Part 2 for the M-Series samples.

FEEDSTOCK

In situ feedstocks for these runs were composite products from the previously described hydrotreater aging runs. Material composites from hydrotreater aging periods 1-4 (Oxy-1), 9-11 (Oxy-2), 15-20 (Oxy-3) and 25-28 (Oxy-4) were stabilized to 125°F atmospheric overhead temperature and provided to the FCR operators as a full-range, rather than fractionated, feedstock.

Properties of these feedstocks are shown in Tables IV-9 through IV-12.

TABLE IV-9

**FLUID CATALYTIC CRACKING
FCR PROCESSING-SAMPLE OXY-1**

| Operating Conditions | | Liquid Properties | | | | |
|-------------------------------|------|-------------------------------------|--------|---------------|---------|---------|
| | | Item | Feed | Total Product | - 600°F | + 600°F |
| Temperature, °F | 995 | °API | 27.4 | 33.6 | 36.6 | 23.5 |
| Cat/Oil Ratio | 13.9 | Carbon, % _w | - | - | - | - |
| C on Regen Cat, % | 0.02 | Hydrogen, % _w | - | - | 12.45 | 11.87 |
| Conversion, Wt % ^a | 44.5 | Nitrogen, % _w | (1.15) | - | (0.73) | (0.87) |
| Closure, Wt % | 96.9 | N _{basic} , % _w | 0.77 | - | 0.356 | 0.234 |
| | | Sulfur, % _w | 0.14 | - | 0.11 | 0.23 |
| | | Oxygen, % _w | - | - | - | - |
| | | Rams C, % _w | - | - | - | 1.70 |
| | | Aromatics, % _w | - | - | - | 44.5 |
| | | GHV, Btu/lb | - | - | - | - |
| | | Distillation, Wt % (°F) by D2887-73 | | | | |
| | | IBP | 333 | - | - | - |
| | | 2 | 373 | - | - | - |
| | | 10 | 453 | - | - | - |
| | | 30 | 569 | - | - | - |
| | | 50 | 661 | - | - | - |
| | | 70 | 766 | - | - | - |
| | | 90 | 876 | - | - | - |
| | | 98 | 943 | - | - | - |
| | | EP | 959 | - | - | - |
| Product Yields, Wt % | | H ₂ | 0.21 | | | |
| | | C ₁ | 0.56 | | | |
| | | C ₂ | 1.18 | | | |
| | | C ₃ | 0.53 | | | |
| | | C ₃ ⁼ | 1.72 | | | |
| | | iC ₄ | 0.60 | | | |
| | | nC ₄ | 0.24 | | | |
| | | C ₄ ⁼ | 2.26 | | | |
| | | C ₅ - 600 | 49.71 | | | |
| | | 600 + | 31.64 | | | |
| | | Coke | 11.35 | | | |

a - Based on the specified cut point above
() Calculated

TABLE IV-10

**FLUID CATALYTIC CRACKING
FOR PROCESSING-SAMPLE OXY-2**

| Operating Conditions | | Liquid Properties | | | | |
|-------------------------------|------|-------------------------------------|---------|---------------|---------|---------|
| | | Item | Feed | Total Product | - 600°F | + 600°F |
| Temperature, °F | 1005 | °API | 26.8 | | 35.7 | 23.3 |
| Cat/Oil Ratio | 6.54 | Carbon, % _w | - | - | - | - |
| C on Regen Cat, % | 0.07 | Hydrogen, % _w | - | - | 11.83 | 11.62 |
| Conversion, Wt % ^a | 47.5 | Nitrogen, % _w | - | - | - | - |
| Closure, Wt % | 95.3 | N _{basic} , % _w | (0.873) | - | 0.387 | 0.258 |
| | | Sulfur, % _w | (0.12) | - | 0.07 | 0.10 |
| | | Oxygen, % _w | - | - | - | - |
| | | Rams C, % _w | (0.69) | - | - | 0.93 |
| | | Aromatics, % _w | - | - | - | 47.4 |
| | | GHV, Btu/lb | - | - | - | - |
| | | Distillation, Wt % (°F) by D2887-73 | | | | |
| | | IBP | 328 | - | - | - |
| | | 2 | 369 | - | - | - |
| | | 10 | 454 | - | - | - |
| | | 30 | 571 | - | - | - |
| | | 50 | 662 | - | - | - |
| | | 70 | 768 | - | - | - |
| | | 90 | 883 | - | - | - |
| | | 98 | 955 | - | - | - |
| | | EP | 986 | - | - | - |
| Product Yields, Wt % | | H ₂ | 0.14 | | | |
| | | C ₁ | 0.51 | | | |
| | | C ₂ | 1.13 | | | |
| | | C ₃ | 0.41 | | | |
| | | C ₃ ⁼ | 1.72 | | | |
| | | iC ₄ | 0.49 | | | |
| | | nC ₄ | 0.20 | | | |
| | | C ₄ ⁼ | 2.36 | | | |
| | | C ₅ - 600 | 49.27 | | | |
| | | 600 + | 29.31 | | | |
| | | Coke | 12.56 | | | |

^a - Based on the specified cut point above

() Calculated

TABLE IV-11

FLUID CATALYTIC CRACKING FCR PROCESSING-SAMPLE OXY-3

| Operating Conditions | | Liquid Properties | | | | |
|-------------------------------|------|-------------------------------------|---------|---------------|---------|---------|
| | | Item | Feed | Total Product | - 600°F | + 600°F |
| Temperature, °F | 990 | °API | 26.8 | 33.2 | 36.5 | 24.2 |
| Cat/Oil Ratio | 7.76 | Carbon, % _w | - | - | - | - |
| C on Regen Cat, % | 0.10 | Hydrogen, % _w | - | - | 12.97 | 11.91 |
| Conversion, Wt % ^a | 46.0 | Nitrogen, % _w | - | - | - | - |
| Closure, Wt % | 91.2 | N _{basic} , % _w | (0.962) | - | 0.441 | 0.288 |
| | | Sulfur, % _w | (0.14) | - | 0.08 | 0.10 |
| | | Oxygen, % _w | - | - | - | - |
| | | Rams C, % _w | - | - | - | 0.85 |
| | | Aromatics, % _w | - | - | - | 47.8 |
| | | GHV, Btu/lb | - | - | - | - |
| | | Distillation, Wt % (°F) by D2887-73 | | | | |
| | | IBP | 318 | - | - | - |
| | | 2 | 367 | - | - | - |
| | | 10 | 452 | - | - | - |
| | | 30 | 570 | - | - | - |
| | | 50 | 662 | - | - | - |
| | | 70 | 768 | - | - | - |
| | | 90 | 877 | - | - | - |
| | | 98 | 945 | - | - | - |
| | | EP | 962 | - | - | - |
| Product Yields, Wt % | | H ₂ | 0.18 | | | |
| | | C ₁ | 0.54 | | | |
| | | C ₂ | 0.93 | | | |
| | | C ₃ | 0.38 | | | |
| | | C ₃ [≡] | 1.55 | | | |
| | | iC ₄ | 0.42 | | | |
| | | nC ₄ | 0.17 | | | |
| | | C ₄ [≡] | 2.03 | | | |
| | | C ₅ - 600 | 44.03 | | | |
| | | 600+ | 33.78 | | | |
| | | Coke | 11.25 | | | |

a - Based on the specified cut point above
() Calculated

TABLE IV-12

**FLUID CATALYTIC CRACKING
FCR PROCESSING-SAMPLE OXY-4**

| Operating Conditions | | Liquid Properties | | | | |
|-------------------------------|-------|-------------------------------------|---------|---------------|---------|---------|
| | | Item | Feed | Total Product | - 600°F | + 600°F |
| Temperature, °F | 1015 | °API | 27.0 | 34.2 | 40.9 | 24.2 |
| Cat/Oil Ratio | 10.65 | Carbon, % _w | - | - | - | - |
| C on Regen Cat, % | 0.03 | Hydrogen, % _w | - | - | 12.50 | 11.94 |
| Conversion, Wt % ^a | 50.62 | Nitrogen, % _w | - | - | (0.57) | (0.64) |
| Closure, Wt % | 101.0 | N _{basic} , % _w | (0.826) | - | 0.29 | 0.25 |
| | | Sulfur, % _w | (0.13) | - | 0.069 | 0.097 |
| | | Oxygen, % _w | - | - | - | - |
| | | Rams C, % _w | (0.71) | - | - | 1.09 |
| | | Aromatics, % _w | - | - | - | 43.6 |
| | | GHV, Btu/lb | - | - | - | - |
| | | Distillation, Wt % (°F) by D2887-73 | | | | |
| | | IBP | 304 | - | - | - |
| | | 2 | 361 | - | - | - |
| | | 10 | 453 | - | - | - |
| | | 30 | 571 | - | - | - |
| | | 50 | 663 | - | - | - |
| | | 70 | 768 | - | - | - |
| | | 90 | 885 | - | - | - |
| | | 98 | 960 | - | - | - |
| | | EP | 992 | - | - | - |
| Product Yields, Wt % | | H ₂ | 0.23 | | | |
| | | C ₁ | 0.73 | | | |
| | | C ₂ | 0.99 | | | |
| | | C ₃ | 0.54 | | | |
| | | C ₃ ⁼ | 1.80 | | | |
| | | iC ₄ | 0.53 | | | |
| | | nC ₄ | 0.27 | | | |
| | | C ₄ ⁼ | 1.96 | | | |
| | | C ₅ - 600 | 48.08 | | | |
| | | 600 + | 30.50 | | | |
| | | Coke | 13.42 | | | |

a - Based on the specified cut point above

() Calculated

DISCUSSION

These runs were the first in which full-range hydro-treater product was charged to the cracker in an effort to take advantage of both the heteroatom removal capability of the unit, as well as to obtain the previously encountered improvement in extractability of the distillate product. Conversions ranged from 44 to 50 weight percent (600°F basis), which were somewhat lower than had been anticipated. Analogous (though slightly less severe) operations had resulted in 57 to 64 weight percent conversions during the M-Series studies charging >600°F feedstock.

Results from these runs demonstrate that full-range crude shale oil hydrotreater products can successfully be processed through the FCC unit. Yields of liquid products, and in particular distillate liquid products, are reduced even at the lowered severity (conversion) effectively imposed in this operation. However, there are advantages still accruing to this mode of operation, in that total heteroatoms in the extraction module charge are reduced by feeding full-range material to the FCC unit, and further, the nitrogen compounds surviving and/or produced during the FCC operation are more amenable to extraction than the blended hydrotreated straight run plus catalytically cracked product produced during the M-Series runs.

RECOMMENDATIONS AND CONCLUSIONS

- Full-range stocks are readily processed on the FCC unit.
- Products from full-range cracking have less heteroatoms (primarily nitrogen) and are more efficiently extracted than distillates which are a blend of cat cracked and straight run hydrotreated materials.
- Liquid yields, and in particular distillate yields, suffer when charging a full-range feed to the FCC unit.

4. MAT TESTS - RECYCLE

SUMMARY

FCC bottoms product, hydrotreated for recycle, has been evaluated over a range of conditions on the microactivity test unit. Conversions ranging 43 to 89 weight percent (600°F basis) were obtained for this material. The product distribution is significantly improved over the original fresh feed basis material as expected, with decreased coke, gas and distillate (400-600) yields, resulting in significantly increased C₅-400 and total distillate (C₅-600) yields at equivalent conversion levels when compared to the analogous fresh feed material. Data from this experimentation confirm the original yield structure projections for this type of recycle material.

OBJECTIVES

The purpose for this study was to determine the yield structure response of hydrotreated recycle material in a rapid manner.

UNIT DESCRIPTION

The equipment utilized for this study was identical to that used during Part 1, fresh feed studies.

EXPERIMENTAL

Experimental procedure was analogous to that used in Part 1.

FEEDSTOCK

The feedstock utilized for this study was M-112 stabilized product from the cycle oil hydrotreater run at 700°F, 1000 psig, 1 LHSV, 3000 SCFB H₂, (Section VII). Properties of this feedstock and source identification data are shown in Table VI-4 under period 2.

RESULTS

Table IV-13 and Figures IV-13 and IV-14 present MAT results for the feedstocks processed.

DISCUSSION

M-112 LCO sample, hydrotreated as described in Section III, was processed over a range of conditions resulting in conversions from 43 to 89 weight percent (600°F basis). As

TABLE IV-13
MILITARY JET FUEL FROM SHALE OIL
PHASE II MAT SUMMARY

| IN NO. | 84 | 85 | 86 | 87 | 90 | 91 | 92 | 93 | 94 | 95 | 96 | 97 |
|--|-------------------|------|-------|------|------|-------|------|------|-------|-------|-------|------|
| FEEDSTOCK | M112 - LCO | | | | | | | | | | | |
| ADDITIONS | 950 | 950 | 1000 | 1000 | 950 | 950 | 1000 | 1000 | 1050 | 1050 | 900 | 900 |
| TEMP., °F | 3.4 | 3.6 | 2.3 | 3.4 | 4.1 | 5.7 | 5.9 | 5.6 | 5.7 | 6.0 | 3.1 | 3.0 |
| CAT./OIL | 13.9 | 13.1 | 22.4 | 13.0 | 12.5 | 7.9 | 7.6 | 8.0 | 8.1 | 7.8 | 14.2 | 14.8 |
| WHSV | 94.7 | 96.2 | 96.0 | 98.8 | 95.9 | 94.8 | 98.1 | 96.4 | 88.5 | 98.8 | 92.4 | 91.9 |
| EST RESULTS | 63.3 | 64.0 | 50.4 | 65.5 | 70.3 | 81.7 | 86.1 | 84.0 | 88.3 | 89.2 | 43.5 | 50.7 |
| RECOVERY, WTZ | 37.2 | 38.1 | 28.4 | 35.3 | 41.5 | 50.6 | 50.9 | 48.0 | 47.4 | 45.4 | 25.2 | 28.3 |
| CONV. OF 600°F+ | 43.4 | 44.6 | 33.2 | 41.2 | 48.5 | 59.1 | 59.5 | 56.1 | 55.4 | 53.0 | 29.4 | 33.1 |
| TOTAL CONV., WTZ | 0.63 | 0.64 | 0.58 | 0.59 | 0.65 | 0.70 | 0.68 | 0.65 | 0.62 | 0.58 | 0.57 | 0.57 |
| to C ₅ -400°F, WTZ | 8.1 | 8.0 | 7.7 | 6.6 | 6.8 | 37 | 2.5 | 1.8 | 0.8 | -0.7 | 6.0 | 7.1 |
| to 400-600°F, WTZ | 8.6 | 8.4 | 8.1 | 7.0 | 7.2 | 3.9 | 2.6 | 1.9 | 0.8 | -0.7 | 6.0 | 7.1 |
| SELECTIVITY | 0.13 | 0.12 | 0.14 | 0.10 | 0.10 | 0.05 | 0.03 | 0.02 | 0.01 | -0.01 | 0.12 | 0.13 |
| to C ₄ MINUS GAS, WTZ | 14.6 | 14.7 | 12.1 | 20.1 | 17.1 | 20.8 | 25.2 | 26.1 | 31.6 | 35.4 | 9.3 | 12.2 |
| to C ₄ *(GAS, WTZ FEED) | 20.6 | 19.5 | 13.3 | 26.4 | 18.8 | 29.1 | 32.0 | 31.2 | 31.2 | 36.6 | 11.8 | 14.7 |
| *(GAS, WTZ RECOVERY) | 21.8 | 20.3 | 16.0 | 26.7 | 19.6 | 30.7 | 32.6 | 32.4 | 35.3 | 37.1 | 12.7 | 16.0 |
| to COKE, WTZ | 3.3 | 3.2 | 2.4 | 3.5 | 4.8 | 6.7 | 7.5 | 8.0 | 8.6 | 9.1 | 3.1 | 3.1 |
| (WTZ C ₄ ON FEED) | 2.7 | 2.6 | 1.9 | 3.0 | 3.9 | 5.4 | 6.3 | 6.6 | 6.4 | 7.6 | 2.4 | 2.4 |
| (WTZ C ₄ ON RECOVERY) | 2.8 | 2.7 | 2.0 | 3.0 | 4.1 | 5.7 | 6.4 | 6.8 | 7.3 | 7.7 | 2.6 | 2.6 |
| UNCONVERTED 600°F+, WTZ | 36.7 | 36.0 | 49.6 | 34.5 | 29.7 | 18.3 | 13.9 | 16.0 | 11.7 | 10.8 | 56.5 | 49.3 |
| UNCONVERTED 600°F+, VOL% | 37.0 | 36.3 | 49.9 | 34.7 | 29.9 | 18.4 | 14.0 | 16.1 | 11.8 | 10.9 | 56.9 | 49.6 |
| PRODUCTS, WTZ RECOVERY | 99.9 | 100 | 100.1 | 100 | 99.9 | 100.1 | 100 | 99.9 | 100.1 | 100 | 100.1 | 100 |
| C ₅ - 600°F RECOVERED, VOL% | 52.0 | 53.0 | 41.3 | 48.2 | 55.7 | 63.0 | 62.1 | 58.0 | 56.2 | 52.3 | 35.8 | 40.6 |

Note: Conversions Determined on a Recovered Weight Basis
* Total Gas, Includes C₅ + Components

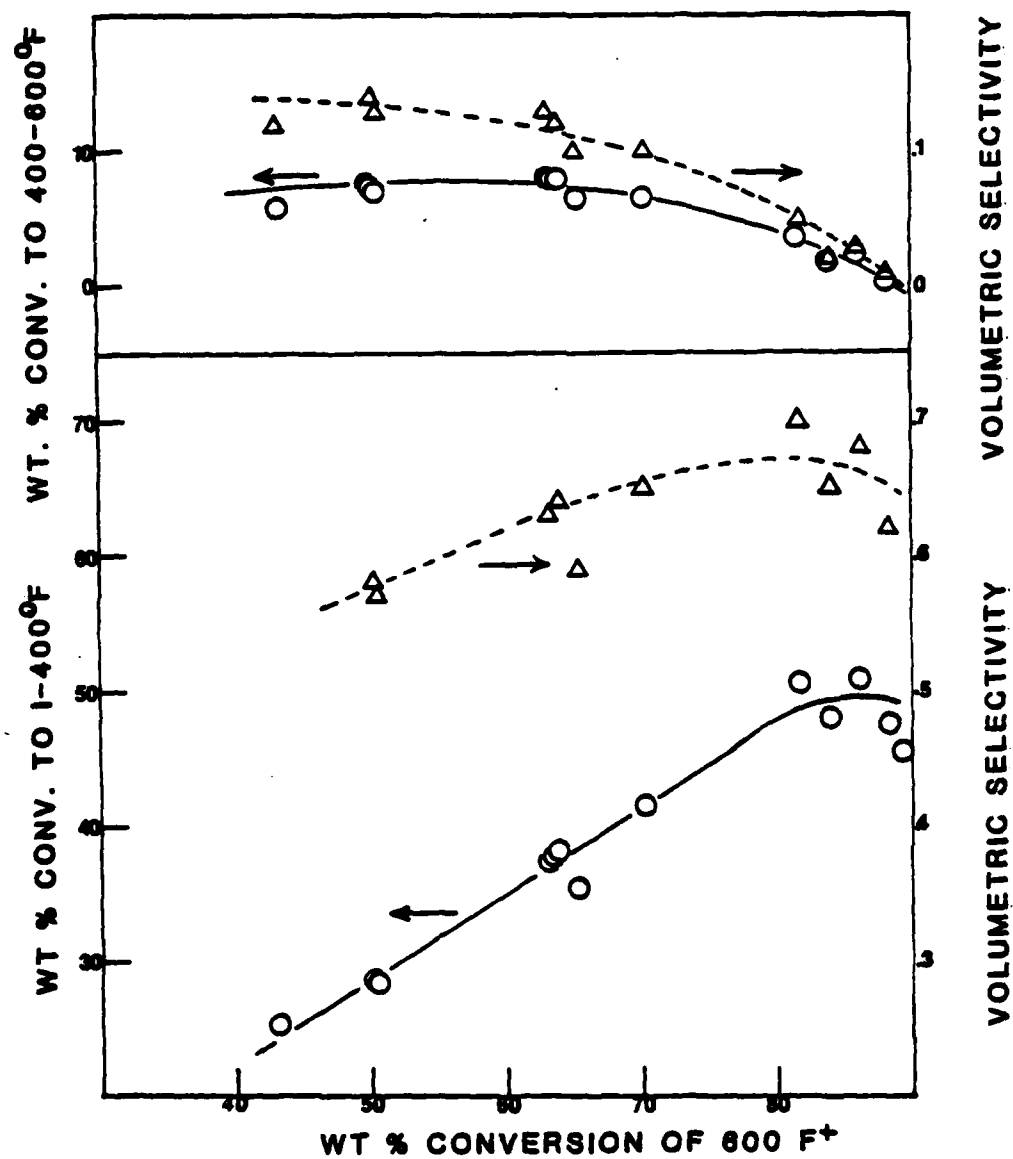


Figure IV-13. Microactivity Test Cracking.
Sample M-112 LCO

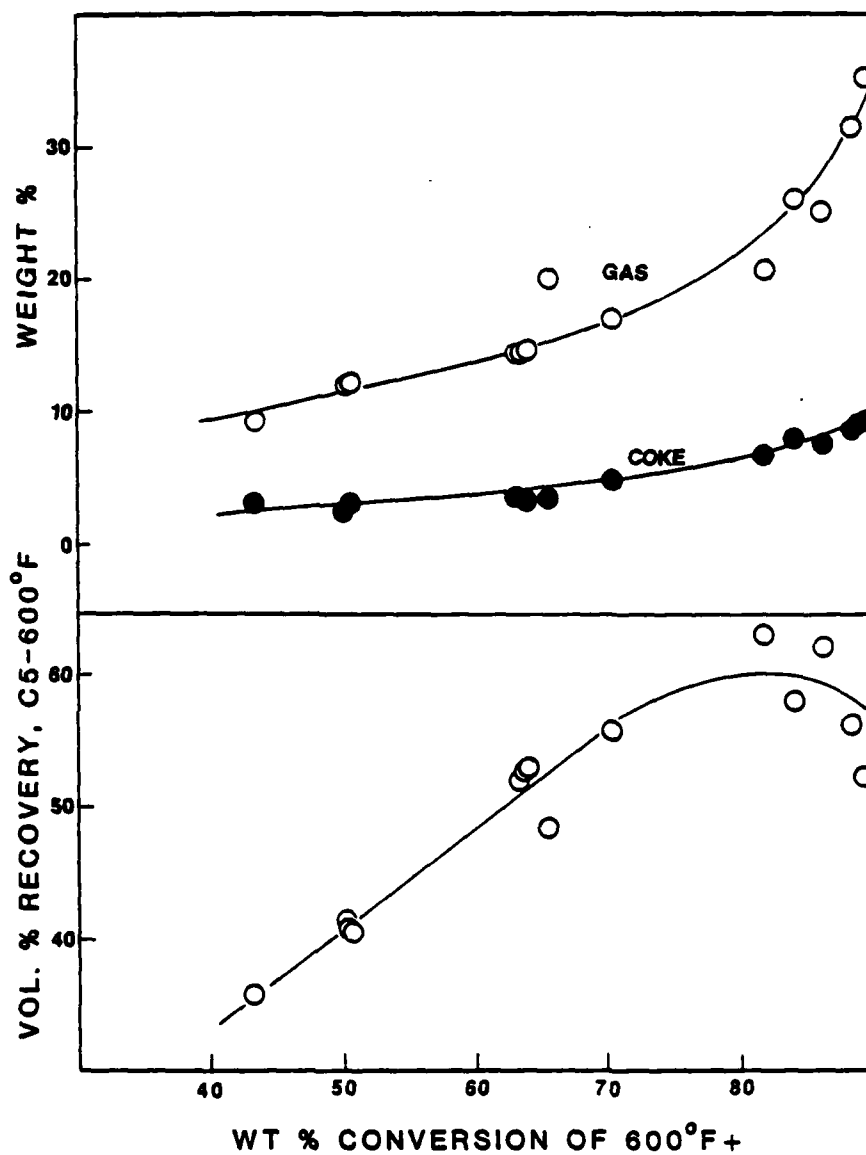


Figure IV-14. Microactivity Test Cracking
Sample M-112 LCO

expected, this recycle material proved to be a superior feedstock to the original fresh feed. Gas, coke and 400-600 distillate product yields were reduced and the C₅-600°F product yield increased dramatically when compared to the corresponding fresh feed sample 11205.

RECOMMENDATIONS AND CONCLUSIONS

- The anticipated increased yield and yield distribution quality were attained from this recycle evaluation.

SECTION V

EXTRACTION

SUMMARY

This work was accomplished using mineral acid as the extraction solvent, and was successful in removing greater than 90 percent of the basic nitrogen content of the feed-stock when performed in a counter-current extraction column.

A screening study (parameter variation) was set up to determine the effects of acid strength, ratio of hydrocarbon to mineral acid and number of stages. This was done batch-wise with in situ retorted shale oil, previously hydrotreated at the crude shale hydrotreater conditions. From this study, the recommended conditions for the remainder of the Phase II extraction work were determined.

The M-Series samples were processed on a continuous countercurrent column and good removal of basic nitrogen was accomplished. Also, there were no detrimental effects of the acid such as gum or sludge formation or polymerization of olefins present in the FCC product. The product raffinates were washed with water.

Large volume samples were then processed for the in situ retorted shale source. The samples were subjected to the same continuous extraction technique as were the M-Series samples. The raffinates were washed in a manner

which effectively removed traces of mineral acid contaminants which would have adverse effects on catalyst activity of the succeeding processing step.

OBJECTIVE

The purpose of nitrogen extraction is to remove a large portion of the basic nitrogen from the naphtha and mid-distillate range straight run and fluid cat cracked shale oil without the use of hydrogen.

MECHANICAL DESCRIPTION

In order to determine the optimal removal of basic nitrogen compounds from the shale oil, a screening study was initiated, varying the acid strength, ratio of hydrocarbon to acid and number of stages involved. This was done in glass separatory funnels. After the conditions were proven to provide the desired results, a continuous countercurrent extraction column was set up for the remainder of the Phase II sample preparations. Residence time and ratio of hydrocarbon to acid were controlled by constant volume bellows feed pumps. Acid strength was controlled by premixing the acid solution feedstock. The column interface level was controlled by the addition of an external standpipe.

After extraction, the raffinate was washed in batch glassware.

CHEMICAL DESCRIPTION

The extraction of nitrogen compounds from the shale oil is effected by an aqueous solution of mineral acid. The concentration of the solution was determined in the screening study to be about 40-50 percent for optimum extraction. This is described in the experimental procedure following.

In order to remove residual acid from the hydrocarbon raffinate after extraction, a dilute aqueous solution of sodium hydroxide was also used. This was followed by water washing to remove residual contaminants.

No catalyst was required.

EXPERIMENTAL PROCEDURE

1. Screening Study

Removal of basic nitrogen compounds from shale oil was accomplished by mineral acid extraction. In order to determine the acid strength and ratio of hydrocarbon to acid which would give optimal removal of basic nitrogen, a series of batch extractions in laboratory glassware was set up. The number of stages was varied also and the removal of basic nitrogen was determined for all points of the matrix.

Independent variables were as follows:

Acid strength was set at four concentrations, 21.55, 41.9, 63.5 and 85 weight percent mineral acid in water.

The ratio of acid (100 percent basis) to hydrocarbon was determined on a weight basis as 0.05, 0.10 and 0.15 per stage, which gave a range of 0.05 to 0.45 as the number of stages varied.

The number of extraction stages was varied from one to three.

The dependent variables analyzed were the removal of nitrogen, the removal of total hydrocarbon, and subjective observations such as "rag" layer or sludge formation, emulsion formation and phase separation. Also recorded was the temperature change due to mixing.

The availability of feedstock limited the set to be done on 400-600°F boiling range material with a check point on IBP-400°F. The feedstock had been previously hydrotreated at conditions anticipated for the crude shale oil hydrotreater. No FCR product was available at the time. The unavailability of cracked feedstock would, therefore, leave unanswered any questions regarding polymerization or hydration of olefins during extraction.

After optimum conditions were determined for the extractions, a continuous countercurrent column was set up for the remainder of the Phase II extraction work.

2. Continuous Extraction of M-Series Samples

The continuous countercurrent extraction column was set up using constant volume bellows feed pumps and an external siphon breaker interface level control. Acid, at

the strength and dosage found from the screening study to be an efficient extraction medium, was pumped to the top feed port of the column while the shale oil to be contacted was pumped into the lower feed port. The feed material was a material balanced blend of IBP-cutpoint from the CSHT and FCR units. The cutpoint was defined as 500°F or 600°F depending upon the final product desired. For two of the samples the straight run material and cracked material were not blended, but contacted separately to determine the effect of the extraction medium on the Bromine Number of the shale oil. A reduction in the Bromine Number, if encountered, would indicate acid catalyzed polymerization of the olefins in the cracked portion of the feedstock.

The column temperature was controlled to the temperature which would aid phase separation but not evaporate or boil off any hydrocarbon. This was controlled by a heat tape wrapped around the column and fitted with a Variac voltage controller and several thermocouples and temperature readouts. After extraction was completed the product raffinate was water washed to remove residual mineral acid. Recoveries of hydrocarbon averaged 88.4 weight percent.

3. Continuous Extraction of In Situ Retorted Shale Oil

Fuel samples were prepared from in situ retorted shale oil by charging the full range CSHT products to the FCC, followed by nitrogen extraction of the IBP-600°F product

fraction. The extractions were performed in the counter-current extraction column in much the same manner as the M-Series samples. After extraction was completed the raffinate was further washed with reagents followed by water washing. The washing steps were incorporated to remove traces of mineral acid which might deactivate catalysts in further processing steps. Washing steps were done in the countercurrent extraction column at a 1 to 1 ratio of hydrocarbon to aqueous phase. The temperature was controlled at about 110°F to aid in phase separation.

EXPERIMENTAL RESULTS

1. Screening Study

The preliminary screening study had the primary objective of predicting the optimum nitrogen removal in the extraction of in situ retorted shale oil with a mineral acid. The feedstock was previously hydrotreated shale oil in the 400°F-600°F boiling range which contained 0.98 weight percent basic nitrogen. The results of the screening test show that the optimum removal of nitrogen occurs at about 40-50 percent acid strength and a nominal 10:1 ratio of hydrocarbon to acid phase and about 3-4 contact stages. (See Tables V-1 and V-2.)

TABLE V-1

**EXPERIMENTAL DESIGN FOR THE
HYDROTREATED IN SITU SHALE OIL DISTILLATE
EXTRACTION PARAMETER STUDY**

| <u>Sequence Number</u> | <u>Acid Strength Percent (Wt.)</u> | <u>Dosage Percent (Wt.)</u> | <u>Stages</u> | <u>Boiling Range</u> |
|----------------------------|--|-------------------------------------|---------------|----------------------|
| 1 | (1) = 21.25 | (1) = 5 | 1,2,3 | (2) = 400-600 |
| 2 | (2) = 41.90 | 1 | 1,2,3 | 2 |
| 3 | (3) = 63.50 | 1 | 1,2,3 | 2 |
| 4 | (4) = 85.00 | 1 | 1,2,3 | 2 |
| 5 | 1 | (2)=10 | 1,2,3 | 2 |
| 6 | 2 | 2 | 1,2,3 | 2 |
| 7 | 3 | 2 | 1,2,3 | 2 |
| 8 | 4 | 2 | 1,2,3 | 2 |
| 9 | 1 | (3)=15 | 1,2,3 | 2 |
| 10 | 2 | 3 | 1,2,3 | 2 |
| 11 | 3 | 3 | 1,2,3 | 2 |
| 12 | 4 | 3 | 1,2,3 | 2 |
| 13 | () | () | 1,2,3 | (1) = I-400 |

Sample No. corresponds to conditions as a suffix of the hydrotreated sample and will be labeled:

EXTRACTION SAMPLE

ie 11104 - 1112

H.T. sequence
Run No. 1 above,
 1 stage

TABLE V-2

DATA SUMMARY - PARAMETER STUDY FOR
BATCH EXTRACTION OF IN SITU HYDROTREATED
SHALE OIL DISTILLATES

| <u>Z. H. EXT.</u> | <u>TOTAL WTZ H.C. EXT.</u> | <u>WT. RATIO TOTAL ACID H.C.</u> | <u>MT'L BAL % CLOSURE</u> | <u>ACID STRENGTH</u> | <u>STAGES</u> |
|-------------------|--------------------------------|--------------------------------------|-------------------------------|--------------------------|---------------|
| 44.6 | 7.1 | 0.05 | 99.1 | 21.25 | 1 |
| 65.5 | 10.7 | 0.10 | 99.1 | 21.25 | 2 |
| 78.1 | 11.7 | 0.15 | 100.9 | 21.25 | 3 |
| 44.6 | 7.4 | 0.05 | 99.8 | 41.90 | 1 |
| 79.0 | 11.8 | 0.10 | 100.0 | 41.90 | 2 |
| 90.2 | 13.4 | 0.15 | 99.9 | 41.90 | 3 |
| 50.0 | 8.9 | 0.05 | 100.0 | 63.5 | 1 |
| 77.8 | 13.5 | 0.10 | 100.0 | 63.5 | 2 |
| 85.0 | 15.6 | 0.15 | 100.0 | 63.5 | 3 |
| 43.7 | 7.7 | 0.05 | 99.7 | 85.0 | 1 |
| 72.9 | 15.0 | 0.10 | 100.0 | 85.0 | 2 |
| 87.4 | 19.9 | 0.15 | 100.0 | 85.0 | 3 |
| 61.6 | 9.4 | 0.10 | 99.9 | 21.25 | 1 |
| 74.5 | 11.3 | 0.20 | 99.9 | 21.25 | 2 |
| 79.4 | 11.7 | 0.30 | 99.9 | 21.25 | 3 |
| 68.5 | 10.4 | 0.10 | 99.9 | 41.90 | 1 |
| 82.1 | 13.3 | 0.20 | 99.9 | 41.90 | 2 |
| 89.2 | 14.6 | 0.30 | 99.9 | 41.90 | 3 |
| 70.6 | 11.4 | 0.10 | 100.0 | 63.5 | 1 |
| 91.2 | 14.8 | 0.20 | 100.0 | 63.5 | 2 |
| 95.4 | 16.5 | 0.30 | 100.0 | 63.5 | 3 |
| 76.2 | 12.7 | 0.10 | 100.0 | 85.0 | 1 |
| 95.9 | 18.5 | 0.20 | ----- | 85.0 | 2 |
| 99.5 | 22.5 | 0.30 | 100.0 | 85.0 | 3 |
| 70.2 | 10.3 | 0.15 | 99.9 | 21.25 | 1 |
| 79.3 | 11.1 | 0.30 | 99.9 | 21.25 | 2 |
| 82.2 | 12.2 | 0.45 | 99.9 | 21.25 | 3 |
| 73.0 | 11.4 | 0.15 | 100.0 | 41.90 | 1 |
| 88.0 | 13.1 | 0.30 | 100.0 | 41.90 | 2 |
| 95.2 | 14.2 | 0.45 | 100.0 | 41.90 | 3 |
| 76.5 | 11.6 | 0.15 | 99.9 | 63.5 | 1 |
| 94.8 | 14.5 | 0.30 | 99.9 | 63.5 | 2 |
| 97.1 | 17.6 | 0.45 | 99.9 | 63.5 | 3 |
| 78.1 | 14.6 | 0.15 | 100.0 | 85.0 | 1 |
| 99.8 | 17.8 | 0.30 | 99.4 | 85.0 | 2 |
| 99.9 | 22.6 | 0.45 | 100.0 | 85.0 | 3 |

The higher concentrations of acid removed slightly more nitrogen from the oil; however, much more hydrocarbon phase was lost to the acid phase in order to do so. Dilute acid tended not to remove a sufficient amount of nitrogen regardless of the number of stages.

After the original batch extraction matrix was completed an extraction of blended IBP-600°F material from the crude shale hydrotreater and FCC units confirmed the applicability of the process. Acid strengths were varied from 21 to 63 percent and 1 through 3 stages were utilized. The nitrogen extracted followed the same trend as with the straight run material. Bromine numbers did not change significantly, indicating little or no polymerization. Again, nitrogen removal was above 90 percent and the optimum conditions were set for continuous extractions on the counter-current column. (See Table V-3.)

Two runs were made to test the results of extraction on four stages of the continuous countercurrent column. The IBP-600°F material blended from CSHT and FCR products was used and the results are shown in Table V-4. The basic nitrogen removal was 94 percent.

2. M-Series

Continuous extraction for the M-Series samples was set up according to the same conditions developed in the preliminary screening study. Samples were available separately of straight run and cracked IBP-cutpoint. These were blended together before the extractions were carried out.

TABLE V-3
EXTRACTION OF BLENDED PRODUCT
DATA SUMMARY

| <u>% N EXT'D</u> | <u>TOTAL WT% HC EXT'D</u> | <u>STAGES</u> | <u>ACID STRENGTH</u> |
|------------------|-------------------------------|---------------|--------------------------|
| 84.5 | 7.3 | 1 | 21.25 |
| 91.2 | 7.8 | 2 | 21.25 |
| 93.6 | 9.1 | 3 | 21.25 |
| 88.2 | 8.1 | 1 | 41.90 |
| 96.4 | 9.1 | 2 | 41.90 |
| 98.1 | 10.6 | 3 | 41.90 |
| 91.9 | 8.7 | 1 | 63.50 |
| 99.0 | 11.0 | 2 | 63.50 |
| 99.5 | 12.9 | 3 | 63.50 |

SAMPLE TREATED:

IBP-600°F FROM CSHT BLENDED WITH
IBP-600°F PRODUCT FROM FCC

TABLE V-4

**CONTINUOUS COUNTERCURRENT
EXTRACTION OF SHALE OIL**

SAMPLE: IBP-600°F FROM CSHT BLENDED WITH
IBP-600°F PRODUCT FROM FCC

| | <u>121</u> | <u>112</u> |
|--------------------------------|------------|------------|
| ACID STRENGTH (WT. %) | 41.9 | 41.9 |
| ACID DOSAGE (WT. ACID: WT. HC) | 1:10 | 1:10 |
| NITROGEN REMOVED (WT. %) | 94.6 | 93.6 |
| RATIO HC/N REMOVED (WT.) | 20.6 | 11.8 |
| BROMINE NO. FEED | 42.2 | 42.0 |
| BROMINE NO. PRODUCT | 45.0 | 39.3 |
| ACTUAL STAGES | 4 | 4 |

Results of these extractions are shown in Table V-5. Products were water washed before further processing.

3. In Situ Retorted Shale Oil

The in situ retorted shale oil, after initial hydro-treatment, FCC processing and appropriate distillation and blending was processed in four separate extractions at conditions determined as optimum for basic nitrogen removal. The continuous extraction column was set up to make use of as many as seven actual stages for mixing and with two for separation of phases. Results are shown in Table V-6. Products were caustic washed with reagent followed by water washing. These steps effectively removed the residual mineral acid to <5 ppm and the other contaminants to <1 ppm in products which were further processed (Section VII).

DISCUSSION OF RESULTS

1. Preliminary Screening Study

The screening study consisted of parameter variation runs in batch separatory funnels in order to establish response data for basic nitrogen extraction. The acid strengths used were 21.25, 41.90, 63.5 and 85.0 percent (weight). The nitrogen extraction generally was favored by high acid strength, however, a large acid to hydrocarbon ratio and many stages would be required, as contact efficiency dropped off above a strength of about 50 percent. A

TABLE V-5

M-SERIES CONTINUOUS EXTRACTION

RESULTS FOR IN SITU SHALE DISTILLATES

| | <u>M-111</u> | | <u>M-112</u> | | <u>M-121</u> | |
|--------------|--------------|-------------|--------------|-------------|--------------|-------------|
| | <u>FEED</u> | <u>RAFF</u> | <u>FEED</u> | <u>RAFF</u> | <u>FEED</u> | <u>RAFF</u> |
| API | - | - | 38.0 | 39.6 | 38.5 | 40.0 |
| BR NO. | 55.9 | 60.0 | 42.0 | 39.3 | 42.2 | 45.0 |
| S, WT. % | - | - | 0.10 | 0.09 | 0.08 | 0.06 |
| N(B), WT. % | 0.704 | 0.125 | 0.700 | 0.045 | 0.623 | 0.04 |
| N REMOVAL % | - | 82.3 | - | 93.6 | - | 92.1 |
| HC REMOVAL % | - | - | - | 7.7 | - | 13.6 |
| SIM D, WT. % | - | - | - | - | - | - |
| IBP | 158 | | 138 | | 128 | |
| 2 | 193 | | 189 | | 164 | |
| 10 | 256 | | 298 | | 277 | |
| 50 | 390 | | 478 | | 456 | |
| 90 | 485 | | 574 | | 553 | |
| 98 | 573 | | 605 | | 575 | |
| ED | 698 | | 663 | | 628 | |

TABLE V-6

CONTINUOUS EXTRACTION RESULTS FOR GC-1 STUDY-IN SITU SHALE DISTILLATES

| | OXY-1 | | OXY-2 | | OXY-3 | | OXY-4 | |
|---------------|-------|-----------|-------|-----------|-------|-----------|-------|-----------|
| | FEED | RAFFINATE | FEED | RAFFINATE | FEED | RAFFINATE | FEED | RAFFINATE |
| API | 36.6 | 37.3 | 36.0 | 37.6 | 36.5 | 38.1 | 40.9 | 40.2 |
| IR NO. | 38 | 42 | 41 | 43 | 46 | 37 | 52 | 47 |
| S, WT, % | 0.07 | 0.07 | 0.07 | 0.09 | 0.09 | 0.09 | 0.08 | 0.08 |
| N(B), WT, % | 0.354 | 0.025 | 0.353 | 0.016 | 0.415 | 0.010 | 0.295 | 0.01 |
| N Removal, % | - | 92.9 | - | 95.5 | - | 97.6 | - | 95.4 |
| HC Removal, % | - | 9.9 | - | 5.4 | - | 3.2 | - | 0.8 |
| SIM D, WT % | | | | | | | | |
| IRP | 221 | - | 223 | 186 | 218 | 211 | 114 | - |
| 2 | 250 | - | 258 | 231 | 243 | 242 | 159 | - |
| 10 | 329 | - | 307 | 297 | 297 | 299 | 229 | - |
| 50 | 476 | - | 456 | 455 | 450 | 449 | 426 | - |
| 90 | 581 | - | 574 | 554 | 562 | 551 | 543 | - |
| 98 | 609 | - | 596 | 576 | 584 | 577 | 574 | - |
| EP | 682 | - | 658 | 582 | 646 | 602 | 586 | - |

plot of weight percent acid strength versus weight percent nitrogen removed (Figure V-1) shows the greater removal of nitrogen as acid strength increases. Figure V-2, however, shows the dramatic decrease in efficiency of removal of nitrogen to total hydrocarbon removed. This indicates a preferred acid strength of about 50 percent or less.

The preliminary batch work was done on 400-600°F boiling range material with a check run using IBP-400°F naphtha. The results indicate that up to 95 percent of the basic nitrogen could be removed using an acid strength in the neighborhood of 50 percent (Figure V-1). A greater denitrogenation could be realized at higher ratios of acid to hydrocarbon, indicating again that multi-stage extraction would be beneficial.

Continuous countercurrent extractions confirmed both the nitrogen removal and the required acid strength. An acid strength of 41.9 percent weight percent was used and resulted in predictable results both in total hydrocarbon removed and in percent basic nitrogen removed. (See Figures V-3 and V-4.)

The dosage of acid to hydrocarbon required was determined by a set of three single stage extractions, using four acid strengths as seen in Figure V-1. Figure V-3 shows that at 41.9 percent acid strength, a 10 percent dosage removes 90 - 95 percent of the basic nitrogen.

The data from the screening study were used to establish the operating conditions for the continuous runs.

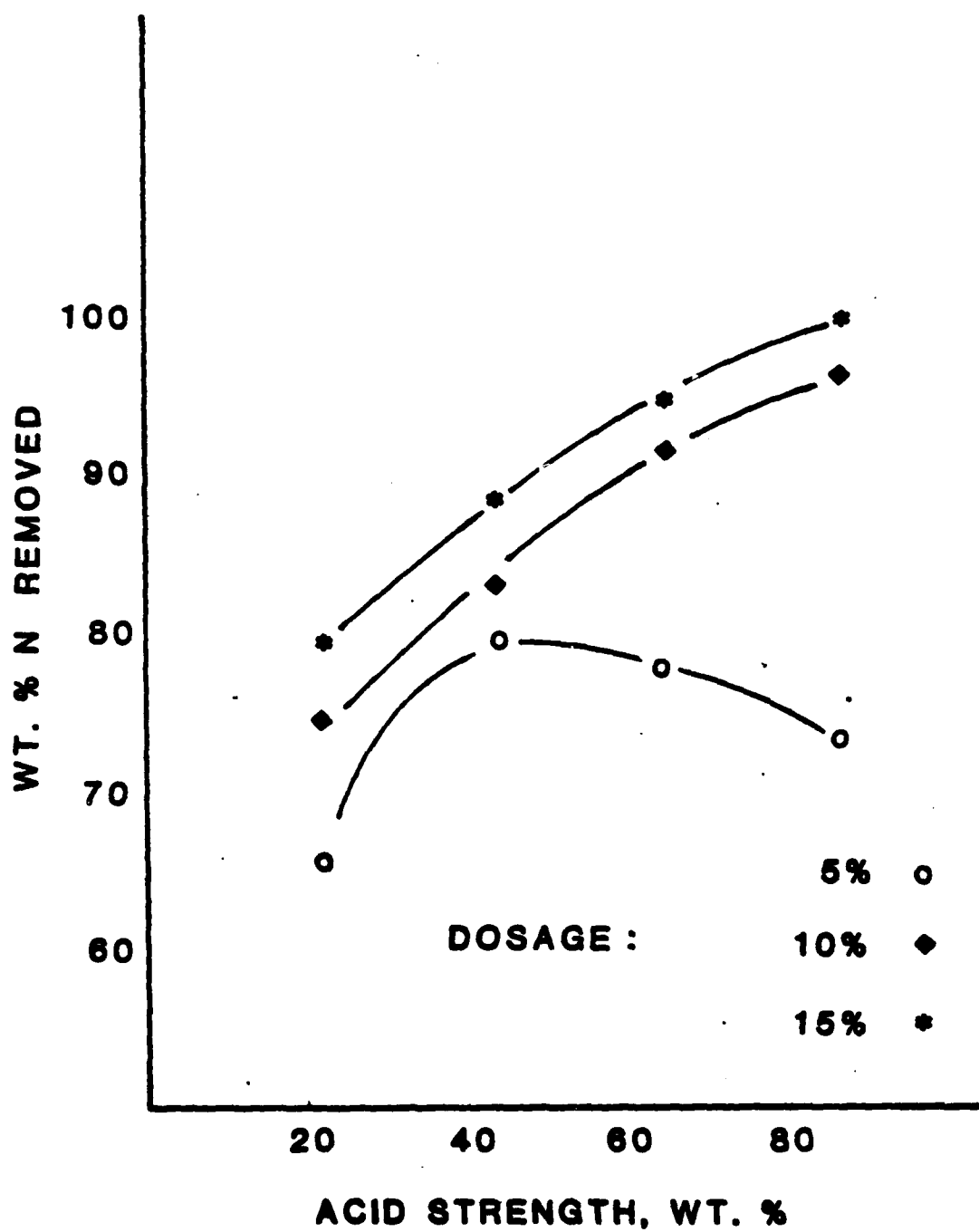


Figure V-1. Batch Extraction Of Basic Nitrogen

10-A129 031

REFINING OF MILITARY JET FUELS FROM SHALE OIL PART II
VOLUME II (IN SITU..(U) ASHLAND PETROLEUM CO KY

33

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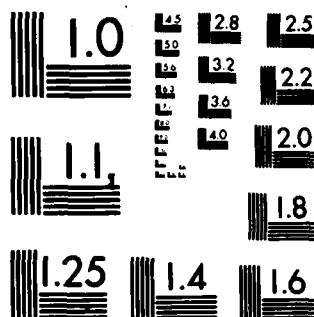
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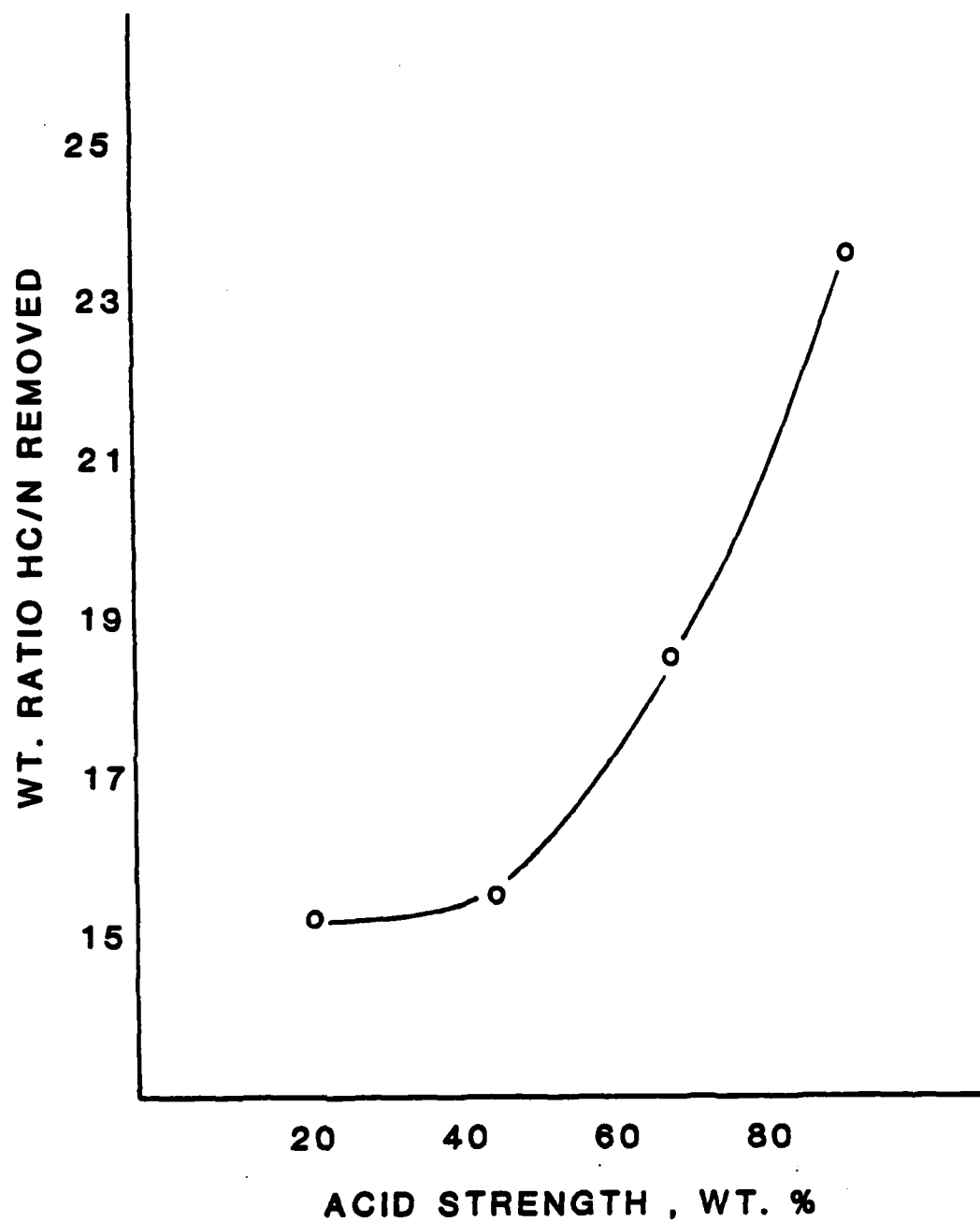


Figure V-2. Ratio Of Hydrocarbon To Nitrogen Removal In Batch Extraction

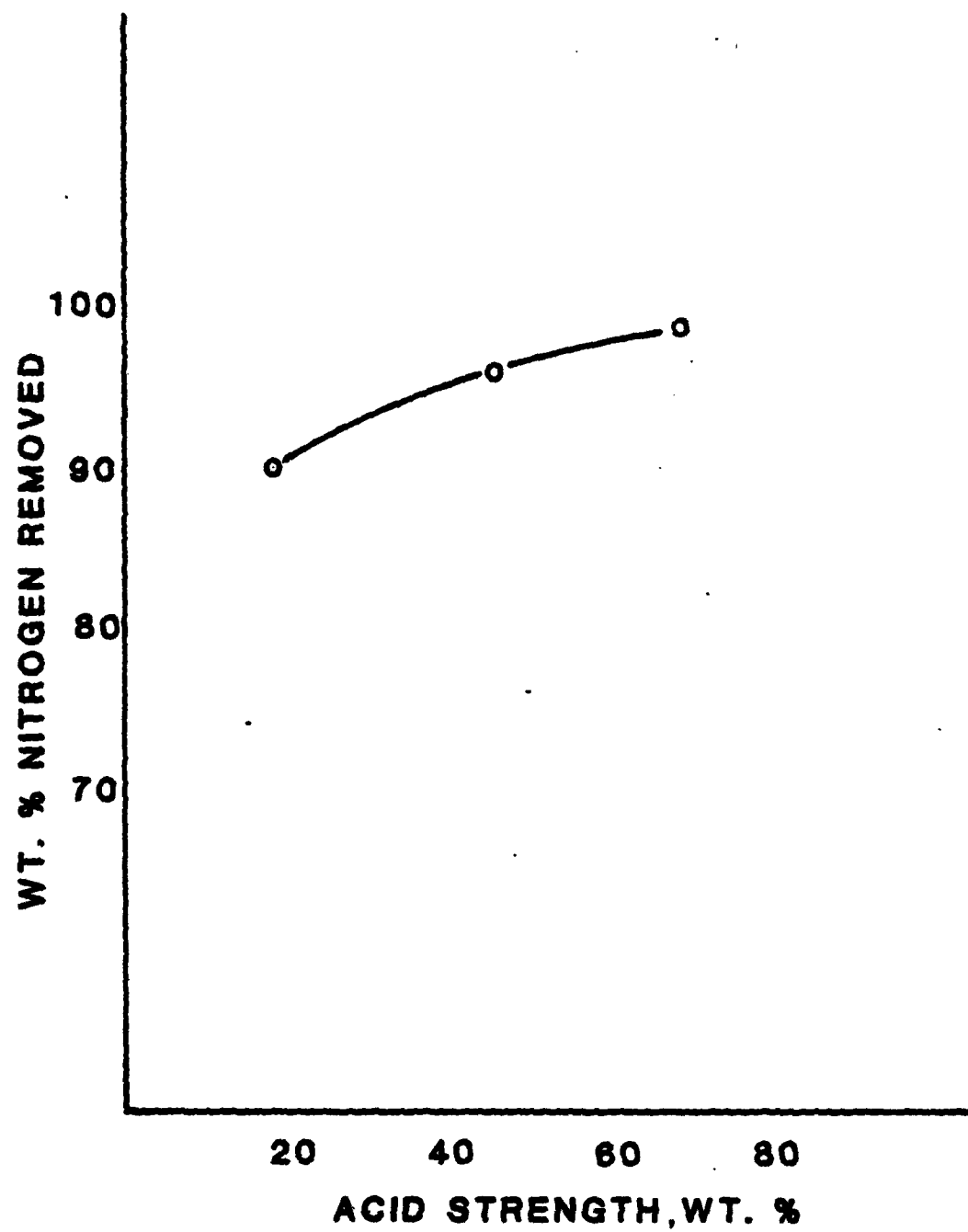


Figure V-3. Continuous Countercurrent Acid Extraction Of Basic Nitrogen.

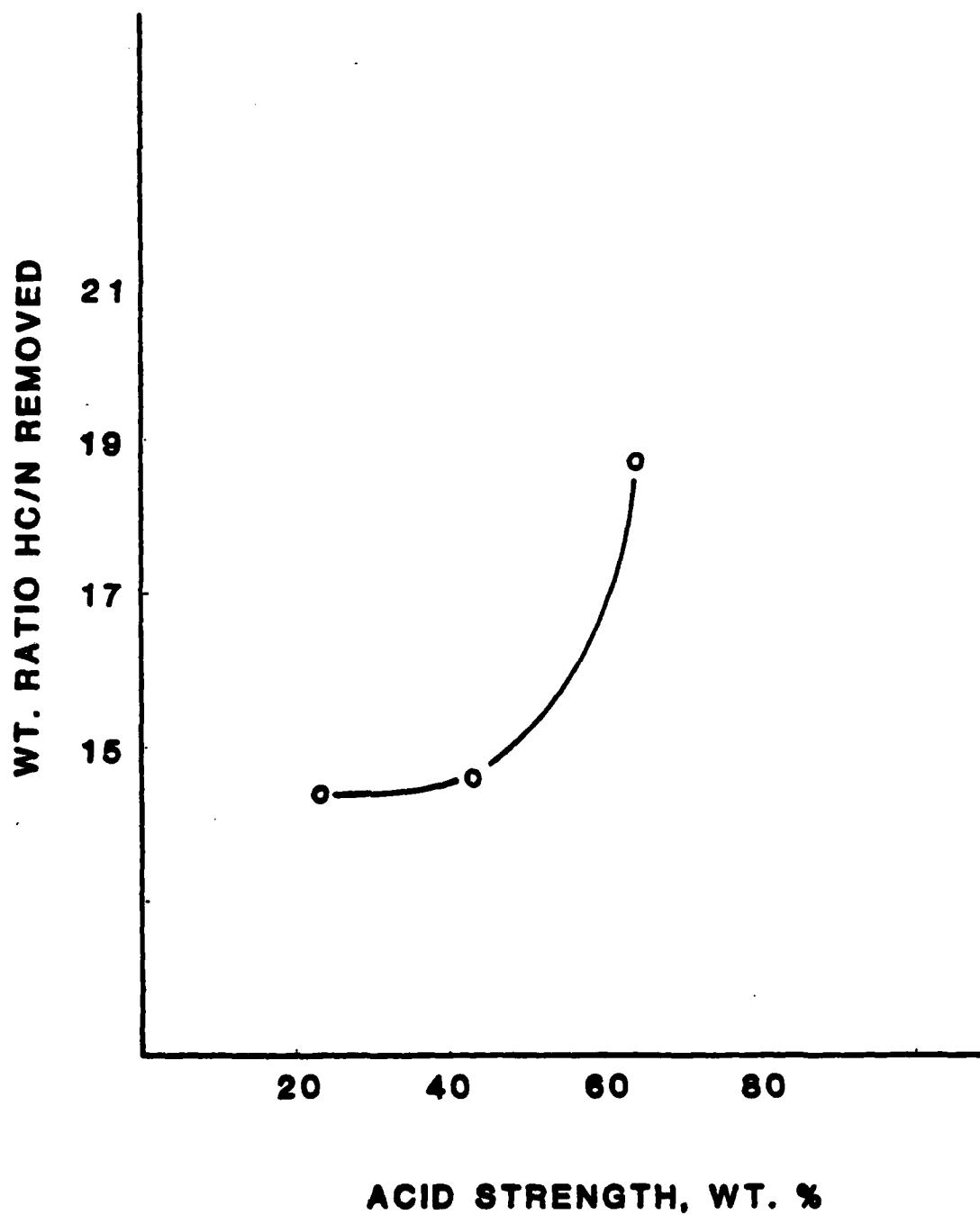


Figure V-4. Ratio Of Hydrocarbon To Nitrogen Removal In Continuous Countercurrent Extraction

2. M-Series

The first series of continuous extractions were conducted on samples in the process scheme. Straight run naphtha (IBP-cutpoint) and FCC naphtha were combined and extracted at conditions determined in the screening study. The continuous extraction utilized up to six actual stages of the countercurrent extraction column and, as a result, showed excellent efficiency in nitrogen removal. The last three lines of Table V-7 show the operating data for the runs and point out that the conditions were held very close to those indicated from the screening runs.

Table V-5 gives the analytical results for the runs showing basic nitrogen removal, Bromine numbers and hydrocarbon recoveries. It should be pointed out that the nitrogen-containing hydrocarbons removed with the aqueous phase are recoverable for further use.

After extraction, the raffinates were washed with water and processed further in the EXTRACTACRACKING scheme.

3. In Situ Retorted Shale Oil

Four samples of in situ retorted shale oil were processed separately on the continuous extraction column. The operating conditions for these runs are shown in Table V-7. The temperature of runs three and four was elevated to effect better phase separation. Acid feed rates were adjusted to give a volumetric ratio close to 10:1 hydrocarbon

TABLE V-7

**OPERATING DATA TABLE FOR
CONTINUOUS EXTRACTIONS OF IN SITU
SHALE OIL DISTILLATES**

| <u>RUN NO.</u> | <u>HC FEED</u> | <u>ACID FEED</u> | <u>HC RCVY</u> | <u>AQ RCVY</u> | <u>VOLUME % CLOSURE</u> | <u>COLUMN TEMP</u> | <u>CONT. TIME (MIN)</u> | <u>ACID STR</u> | <u>HC: ACID RATIO (WT.)</u> |
|----------------|--------------------|----------------------|--------------------|--------------------|-----------------------------|------------------------|---------------------------------|---------------------|---------------------------------|
| OXY-1 | 100 | 16 | 90.1 | 25.1 | 99.3 | 85 | 21 | 41.9 | 6.2 |
| OXY-2 | 100 | 15.5 | 94.6 | 20.9 | 100.0 | 87 | 21 | 41.9 | 6.5 |
| OXY-3 | 100 | 16.6 | 96.8 | 19.8 | 100.0 | 125 | 21 | 41.9 | 6.0 |
| OXY-4 | 100 | 16.6 | 99.2 | 17.5 | 100.1 | 145 | 21 | 41.9 | 6.0 |
| M-111 | Aborted | | | | | | | | |
| M-112 | 100 | 13.0 | 92.3 | 20.8 | 100.1 | 86 | 21 | 41.9 | 7.7 |
| M-121 | 100 | 12.2 | 86.3 | 25.9 | 100.0 | 86 | 21 | 41.9 | 8.2 |

* Note: All units are wt% unless otherwise specified

to acid phase. The actual weight ratios are also reported in the operating data. Contact time was approximately 21 minutes.

Removal of basic nitrogen was in the 95 percent range as shown in Table V-6. Hydrocarbon removal was less than 10 percent, indicating optimum conditions. The conditions of acid strength and dosage as set up during the preceeding work continued to prove satisfactory. No significant change occurred in Bromine numbers, indicating little or no effect upon olefin content.

The temperature of the raffinate was allowed to go up to 145° in the fourth run, which proved too high. The remaining experiments were conducted at about 87 to 90°F. For good continuous phase separation and higher throughput, it was determined that the temperature should be controlled at about 100°F or slightly above. Care was taken to keep it below the IBP of the feedstock, however.

Products from these runs were subjected to countercurrent washing with reagent and then deionized water to prevent residual contaminants from deactivating the catalyst during guardcase hydrotreating.

CONCLUSIONS

From the screening study it was determined that significant basic nitrogen could be extracted from the previously hydrotreated shale oil. Conditions were established for future continuous processing as follows:

| | |
|---------------|--------|
| Acid Dosage | 1:10 |
| Acid Strength | 40-60% |
| Number Stages | >2 |

The M-Series samples were successfully extracted on the continuous column utilizing only four contact stages. Predictable basic nitrogen removal of up to 95.8 percent was accomplished.

The in situ samples were also extracted with up to 99 percent removal of basic nitrogen. These samples were also caustic washed and water washed for removal of trace amounts of mineral acid and sodium.

In the cases involving cracked naphtha, no problems were encountered due to potential polymerization or gum formation.

Operations at temperatures around 100°F suggest better phase separation and no "cuff" layer formation.

Conditions recommended for Phase III Pilot Plant Preparation of samples are as outlined in Table V-8.

TABLE V-8
OPERATING PARAMETERS FOR EXTRACTION

| | <u>PHASE II</u> | <u>PHASE III (RECOM)</u> |
|-------------------------------------|-----------------|--------------------------|
| <u>ACID EXTRACTION</u> | | |
| Column Diameter, in. I. D. | 1.0 | 2.0 |
| Hydrocarbon Feed Rate, ml/min | 22.0 | 115.0 |
| Acid Feed Rate, ml/min | 2.2 | 15.0 |
| Acid Strength, wt. % | 41.9 | 41.9 |
| Residence Time, min. | 21 | 13 |
| Column Temperature, °F | 75 - 150 | 110 - 115 |
| <u>H₂O Washing</u> | | |
| Hydrocarbon Feed Rate, ml/min | -* | 300 |
| H ₂ O Feed Rate, ml/min. | - | 300 |
| Column Temperature, °F | - | 110 |

*Batchwise

SECTION VI

RECYCLE OIL HYDROTREATING

SUMMARY

A total of four nominal twelve hour material balance periods were performed during the bench scale cycle oil hydrotreating of the M-Series in situ shale oil indicating that this product could be effectively hydrotreated. The data collected show that at operating conditions of 1400 psig and 700°F, desulfurization can reach at least 87 percent, while denitrogenation can reach at least 71 percent. The product samples easily met all fuel oil military specifications analyzed except pour point.

OBJECTIVES

The main objective of this series of cycle oil hydrotreating runs was to provide parameter response data for optimization of hydrotreating of FCC bottoms produced via the EXTRACTACRACKING process. These studies were intended to verify that the FCC bottoms could be hydrotreated to produce a lowered nitrogen, low-sulfur fuel oil, in addition to providing an upgraded recycle oil stream to the FCC unit if desired.

FEEDSTOCKS

The feedstocks for the cycle oil hydrotreating runs on in situ shale oil were coded M-112 and M-121. In the experimental scheme of the EXTRACTACRACKING process the M-112 feedstock had been hydrotreated at 650°F, 1000 psig,

2 LHSV and a 3000 SCFB H_2 rate with a cobalt molybdate catalyst, fractionated into a 600°F+ cut, sent to an FCC unit where it was cracked and finally fractionated into a 600°F+ cut. The M-121 feedstock was hydrotreated at the same conditions although with a nickel molybdate catalyst. This feedstock was then also fractionated into a 600°F+ cut, cracked in an FCC unit and once more fractionated to a 600°F+ cut. The available properties of the respective feedstocks are given in Tables VI-1 and VI-2.

Due to the small equipment sizes used, problems with catalyst fines were encountered.

EQUIPMENT

A nominal one-inch trickle flow laboratory reactor was used in the cycle oil hydrotreating studies. The reactor and the equipment set-up corresponded essentially to that used in the M-Series crude shale hydrotreating study and is shown schematically in Figure VI-1. The main differences between this set-up and that used in other studies were: (1) the absence of a guardbed for catalyst protection, (2) a different method of regulating reactor pressure and (3) the absence of a mist separator in the gas flow stream after liquid collection. Temperature control for the reactor itself was provided in this instance by 3 PID controllers driven by external skin temperature thermocouples. Heat lamps and heating tapes were used to keep the feed flowing to the reactor and avoid ramp problems.

TABLE VI-1

**FEED CHARACTERIZATION: CYCLE OIL
HYDROTREATING - SAMPLE M-112**

| Properties: | | Distillation, °F: | |
|--------------------------------|-------|--------------------------|---------------|
| °API | 23.4 | Wt % By | D-2887 |
| Carbon, Wt % | - | IBP | 600 |
| Hydrogen, Wt % | - | 2 | 602 |
| Nitrogen, Wt % | - | 10 | 620 |
| Basic Nitrogen, Wt % | - | 30 | 661 |
| Sulfur, Wt % | - | 50 | 711 |
| Oxygen, Wt % | 0.178 | 70 | 773 |
| Ramsbottom Carbon, Wt % | - | 90 | 856 |
| Aromatics, Wt % | - | 98 | 922 |
| | | EP | 935 |

TABLE VI-2

**FEED CHARACTERIZATION: CYCLE OIL
HYDROTREATING - SAMPLE M121**

Properties:

| | |
|--------------------------------|--------|
| °API | 22.5 |
| Carbon, Wt % | - |
| Hydrogen, Wt % | - |
| Nitrogen, Wt % | (0.93) |
| Basic Nitrogen, Wt % | - |
| Sulfur, Wt % | 0.12 |
| Oxygen, Wt % | 0.218 |
| Ramsbottom Carbon, Wt % | 0.98 |
| Aromatics, Wt % | - |

Distillation, °F:

| Wt % By | D-2887 |
|----------------|---------------|
| IBP | 530 |
| 2 | 548 |
| 10 | 603 |
| 30 | 652 |
| 50 | 702 |
| 70 | 766 |
| 90 | 853 |
| 98 | 921 |
| EP | 939 |

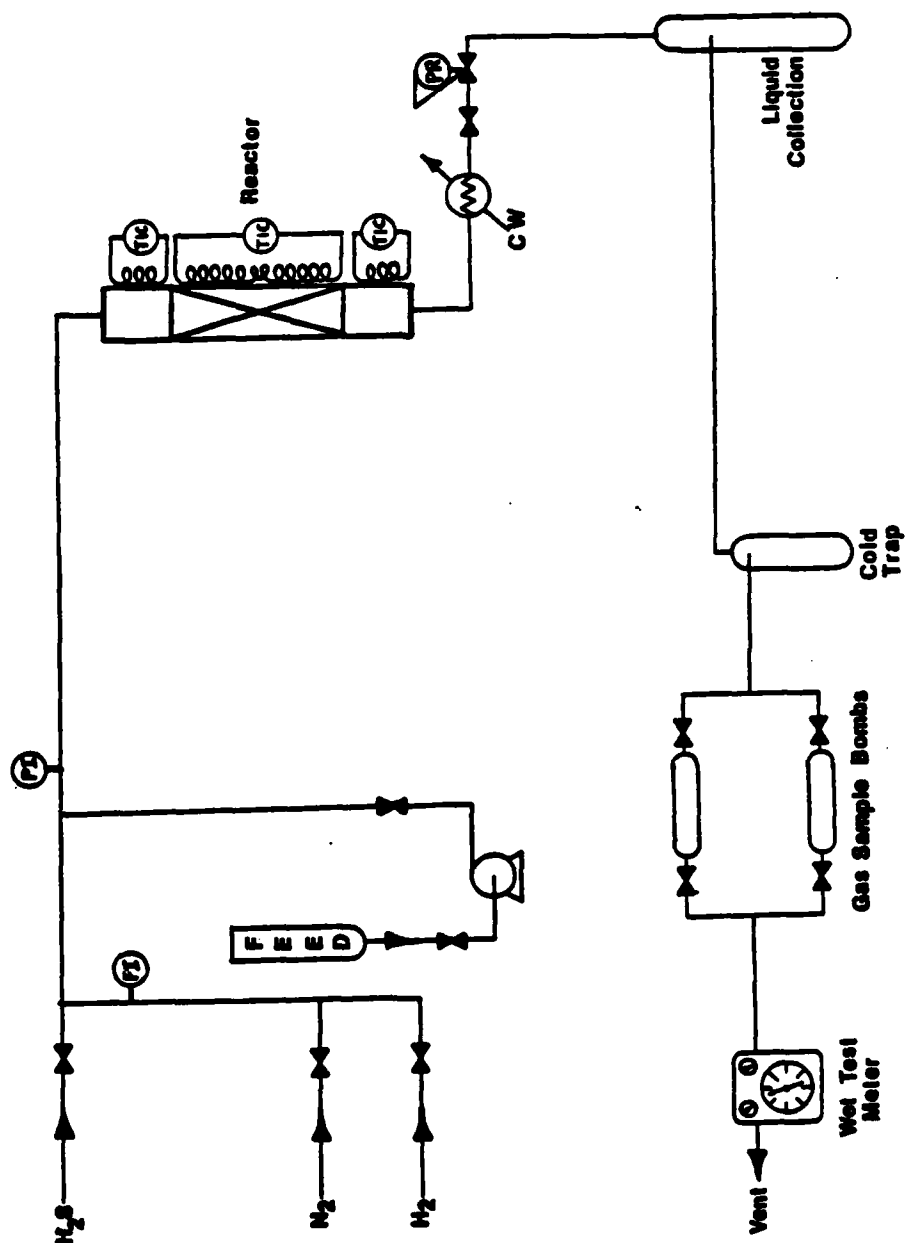


Figure VI-1. Cycle Oil Hydrotreater Configuration

EXPERIMENTAL PROCEDURE

The desired nominal operating conditions and scheduling of test periods for the cycle oil hydrotreating studies on an in situ shale oil were as given in Table VI-3. The M-112 cycle oil feedstock was hydrotreated at constant nominal operating conditions of 1000 psig, 1 LHSV, 3000 SCFB hydrogen rate over a catalyst charge of 50cc of a nickel molybdate catalyst and at temperatures of 650°F and 700°F before the feed was exhausted. The M-121 cycle oil feedstock was hydrotreated at 1400 psig, 1 LHSV, 3000 SCFB hydrogen rate over a catalyst charge of 50cc of a nickel molybdate catalyst and at temperatures of 650°F and 700°F before this feed was likewise exhausted.

The reactor for each feedstock was packed first with tabular alumina. Next the catalyst bed, consisting of 50cc of catalyst and 50cc of Ottawa sand, was centered in the reactor with the sand and catalyst added alternately in 10cc increments. The remaining section of the reactor was packed with tabular alumina.

Before each feedstock was fed to the reactor, the reactor was pressure checked to roughly 100 psig above the nominal operating pressure with both nitrogen and hydrogen. The catalyst was presulfided with H_2S at bottle pressure up to 50°F over the maximum desired run temperature or at 800°F. After the reactor had cooled and the hydrogen flow rate had been set to 3000 SCFB, the reactor was pressurized to the appropriate run pressure. Feed was initiated and

TABLE VI-3

**M-SERIES OPERATING CONDITIONS FOR
RECYCLE HYDROTREATING OF IN SITU OIL**

| | | |
|-------------------|----------|----------|
| SAMPLE ID | M-112-CO | M-121-CO |
| API | 23.4 | 22.5 |
| SHALE OIL TYPE | In Situ | In Situ |

**CONSTANT
OPERATING
CONDITIONS:**

| | | |
|---------------------------|-------|-------|
| Pressure, PSIG | 1000 | 1400 |
| LHSV, Hr-1 | 1 | 1 |
| H ₂ Rate, SCFB | 3000 | 3000 |
| Catalyst | Ni/Mo | Ni/Mo |
| Catalyst Charge, CC | 50 | 50 |

PERIOD (HRS) TEMPERATURE, °F

| | |
|----|-------------------------|
| 12 | Lineout, 650°F |
| 24 | Material Balance, 650°F |
| 36 | Lineout, 700°F |
| 48 | Material Balance, 700°F |
| 60 | Lineout, 750°F |
| 72 | Material Balance, 750°F |
| 84 | Material Balance, 750°F |

the entire system was slowly brought up to the desired operating conditions, starting with a reaction temperature of 650°F for each feedstock. Conditions were monitored continuously and recorded hourly to maintain them at the levels delineated above. Twelve-hour lineout periods were allowed between tests as indicated in Table VI-3. Each test period consisted of a nominal twelve-hour material balance, but since the sample quantities were limited, operations were carried through exhaustion of sample rather than end of time sequence. Where end of feed occurred during a lineout, or very early in a material balance, the last full material balance was extended to end of feed.

The samples for each material balance were stabilized on an Oldershaw column. This stripping was performed for two to three hours at atmospheric pressure while maintaining a pot temperature greater than 300°F.

RESULTS

The operating results for the cycle oil hydrotreating studies on an in situ shale oil are presented in Table VI-4. These results include material balances based on weight percent of feed for the test lengths given. The operating conditions listed were averaged over the test period.

On the same table are listed the available product properties for the stabilized or stripped full range hydro-treated product. The results for the M-121 feedstock led to the plots of percent desulfurization and percent denitrogenation versus reaction temperature shown in Figures

TABLE VI-4

**CYCLE OIL HYDROTREATING:
IN SITU SHALE OIL**

| Feed | M- | 112 | 112 | 121 | 121 |
|-----------------------------|-----------------|--------|-------|--------|--------|
| Period | TEST LENGTH, Hr | 1 / 12 | 2 / 9 | 3 / 12 | 4 / 18 |
| OPERATING CONDITIONS | | | | | |
| Temperature, °F | | 650 | 700 | 650 | 700 |
| Pressure, PSIG | | 1000 | 1000 | 1400 | 1400 |
| LHSV, Hr ⁻¹ | | 1 | 1 | 1 | 1 |
| H ₂ Rate, SCFB | | 3112 | 3020 | 2954 | 2820 |
| MATERIAL BALANCE | | | | | |
| Weight Percent of Feed | | | | | |
| Feed | | 100 | 100 | 100 | 100 |
| H ₂ In | | 5.2 | 5.0 | 5.0 | 4.7 |
| Subtotal In | | 105.2 | 105.0 | 105.0 | 104.7 |
| H ₂ O | | (0.20) | - | (0.25) | (0.25) |
| NH ₃ | | (-) | - | (0.45) | (0.80) |
| H ₂ S | | (-) | - | (0.10) | (0.11) |
| H ₂ Out | | 4.7 | - | 4.5 | 3.0 |
| C ₁ | | - | - | 0.10 | 0.10 |
| C ₂ | | 0.03 | - | - | 0.80 |
| C ₃ | | 0.04 | - | 0.10 | 0.70 |
| C ₄ | | 0.03 | - | 0.15 | 0.60 |
| C ₅ | | 0.04 | - | 0.04 | 0.50 |
| Stabilized Liquid | | 105.04 | 96.7 | 99.60 | 96.70 |
| Subtotal | | - | - | 105.29 | 103.56 |
| Closure | | - | - | 100.3 | 98.9 |
| Hydrogen Consumption, SCFB | | 301 | - | 295 | 1031 |
| PRODUCT PROPERTIES | | | | | |
| °API | | 26.0 | - | 26.2 | 27.0 |
| Sulfur, Wt % | | 0.035 | - | 0.029 | 0.016 |
| Nitrogen, Wt % | | 0.61 | - | 0.56 | 0.28 |
| Oxygen, Wt % | | - | - | - | - |
| Viscosity 100°F, cSt | | 21.63 | - | 20.47 | 16.68 |
| " 210°F, cSt | | 3.73 | - | 3.59 | 3.27 |
| Pour Point, °F | | 60 | - | 55 | 55 |

VI-2 and VI-3. Simulated distillations were run on the full range product materials and are also given in Table VI-5.

DISCUSSION OF RESULTS

Operation of the bench scale cycle oil hydrotreater to hydrotreat M-Series in situ shale oil went very smoothly. The only problems encountered during the cycle oil hydrotreating step were insufficient quantities of feedstocks as well as insufficient analytical characterization of feedstocks and products.

Even with this shortage of data, the M-121 runs indicate that sulfur and nitrogen removals were quite good. With the reaction carried out at 650°F, 1400 psig, the level of desulfurization was about 76 percent and the level of denitrogenation was 40 percent. With the reactor at 700°F and 1400 psig pressure, desulfurization had increased to roughly 87 percent and denitrogenation had jumped to almost 71 percent.

Since part of the product stream from the cycle oil hydrotreater represents net fuel oil product, examination of the military specifications for fuel oil shows that all analyzed product streams easily surpass the maximum sulfur level of 3.5 weight percent, with the highest sulfur level in any of the product samples at 0.035 weight percent. The API gravity of all product samples is well above the minimum allowed, while the viscosity is well below the maximum

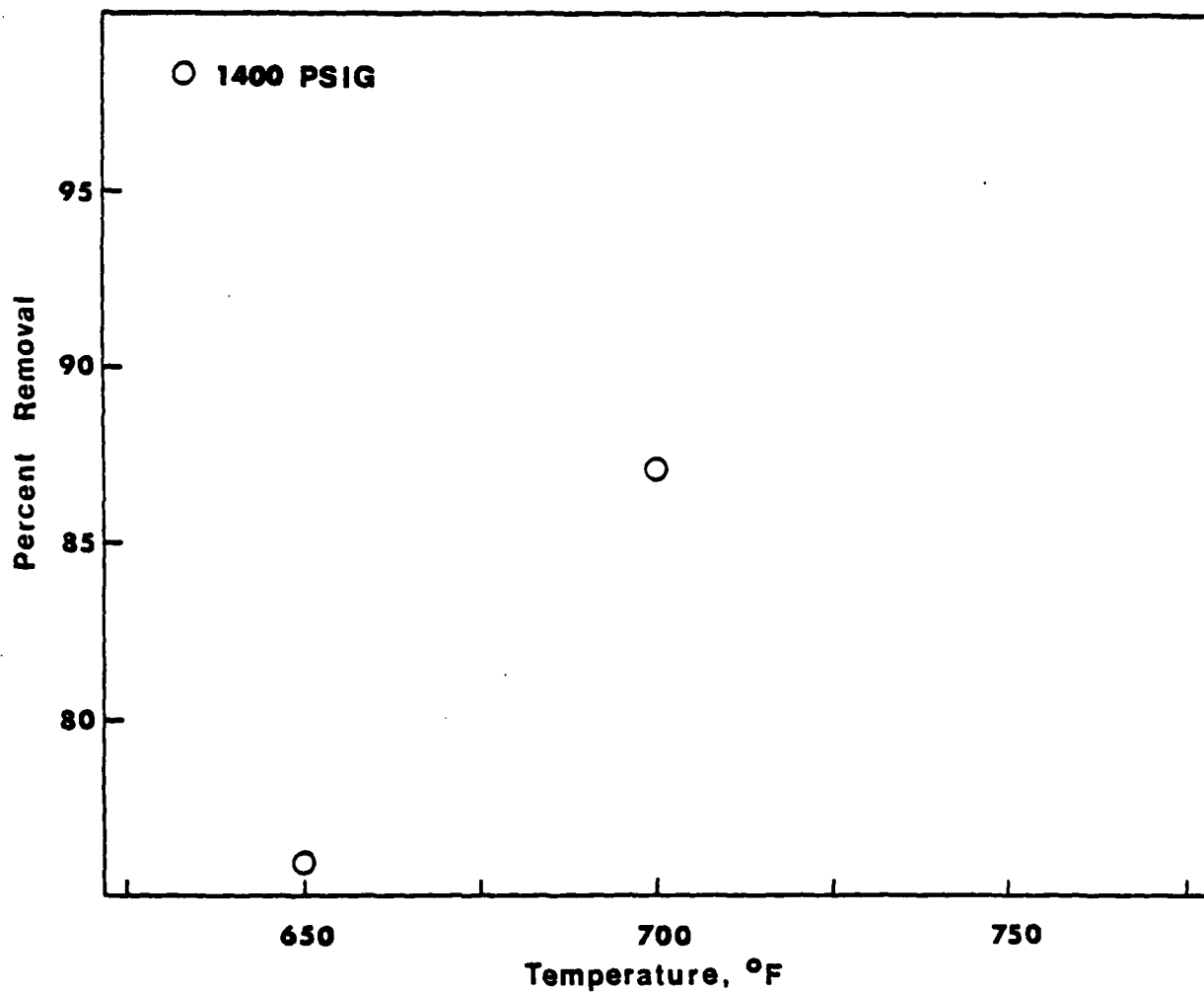


Figure VI-2. Cycle Oil Hydrotreating - In Situ Shale Oil - Temperature Dependence Of Desulfurization At 1 LHSV

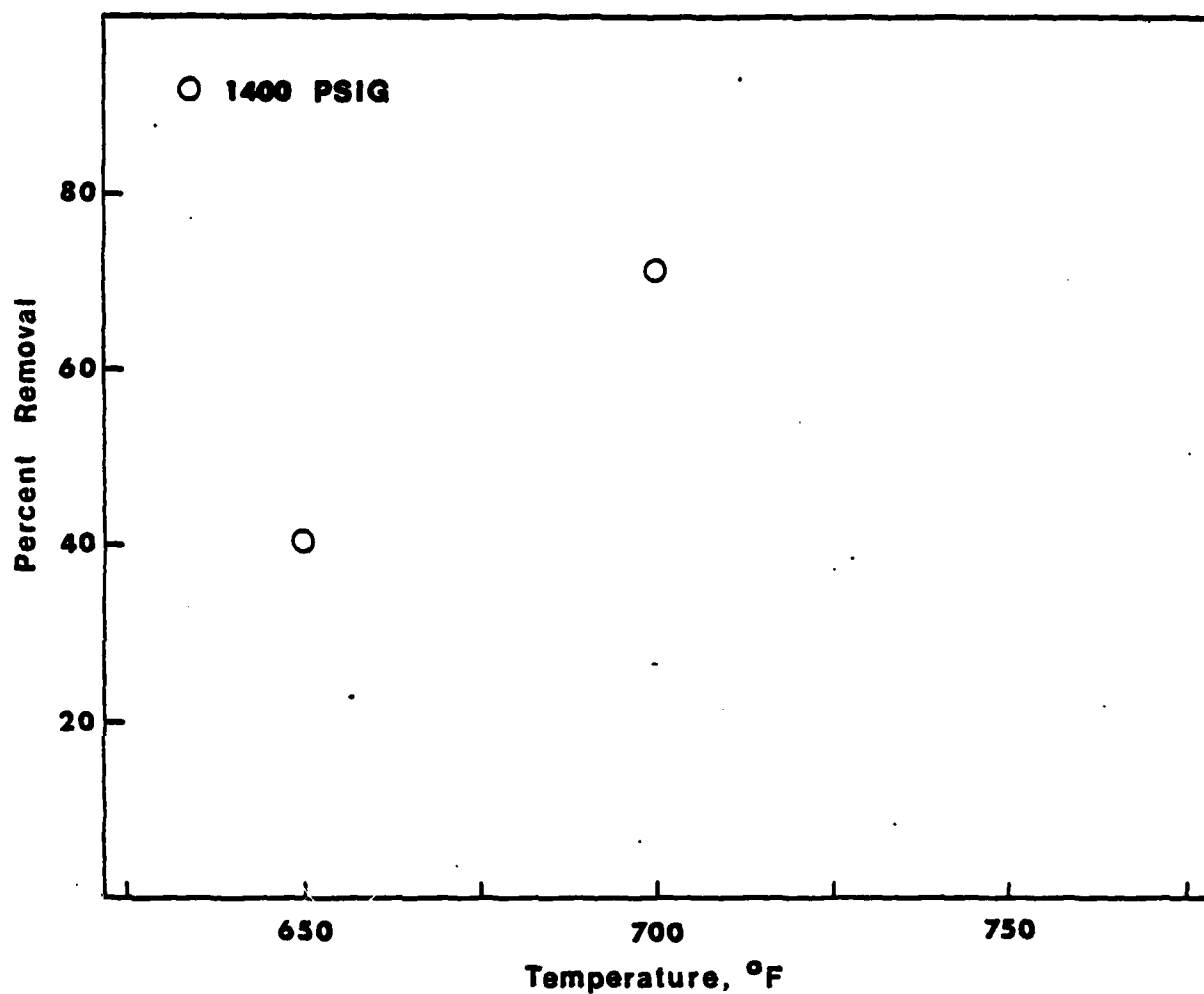


Figure VI-3. Cycle Oil Hydrotreating - In Situ Shale Oil -Temperature Dependence Of Denitrogenation At 1 LHSV

TABLE VI-5

**DISTILLATION OF FULL RANGE CYCLE OIL
HYDROTREATED IN SITU SHALE OIL**

| SAMPLE | M-112 | M-121 | M-121 |
|------------------------------|-----------|-----------|-----------|
| OPERATING CONDITIONS | | | |
| Temperature, °F | 650 | 650 | 700 |
| Pressure, PSIG | 1000 | 1400 | 1400 |
| LHSV, Hr ⁻¹ | 1 | 1 | 1 |
| H ₂ Rate, SCFB | 3112 | 2954 | 2820 |
| D2887-73 DISTILLATION | | | |
| Wt% | °F | °F | °F |
| IBP | 431 | 364 | 391 |
| 2 | 513 | 476 | 466 |
| 10 | 592 | 579 | 565 |
| 30 | 648 | 645 | 634 |
| 50 | 703 | 697 | 689 |
| 70 | 773 | 761 | 756 |
| 90 | 874 | 854 | 852 |
| 98 | 976 | 929 | 935 |
| EP | * | 949 | 963 |

* Beyond temperature limit of distillation device

allowed. Carbon residue in a fuel oil stream from the cycle oil hydrotreater should also present no problem. The only property evaluated that did not meet specifications was the pour point which was 40 to 45°F over the allowed maximum. This is due to the known high paraffin content of the products. Addition of conventional pour depressants should alleviate this problem.

CONCLUSIONS/RECOMMENDATIONS

The results of the operation of the bench scale cycle oil hydrotreater on the M-Series in situ shale oil show that this shale, processed as indicated, can be effectively hydrotreated. Data obtained indicate that even at the relatively mild operating conditions of 650°F and 1400 psig, the M-121 samples showed a desulfurization of 76 percent and a denitrogenation of 40 percent. Increasing the reaction temperature increases the levels of heteroatom removal and the maximum levels of desulfurization and denitrogenation obtained were 87 and 71 percent, respectively, at 700°F and 1400 psig.

All military specifications on fuel oil, including sulfur content, carbon residue, API gravity and viscosity, can easily be met by the M-Series in situ shale oil product from the cycle oil hydrotreater. The pour point does not meet specifications due to the high paraffin content of the product. Further processing of the product stream should not be difficult and should be considered.

SECTION VII

GUARDCASE HYDROTREATING

The guardcase hydrotreater is provided in the EXTRACT-ACRACKING process for final removal of trace quantities of sulfur, nitrogen, oxygen and/or metallic contaminants. This process section provides an ultrapure feedstock for any further processing required downstream.

Two sets of studies were provided during Phase II. In the first study, two samples (from the previously described M-Series) were processed at constant (projected) required conditions. In the second, incremental severity increases were provided to define minimum required severity for a 1 ppm sulfur and nitrogen product, followed by roughly 100 hours or more at single conditions to evaluate catalyst stability.

Products from these studies were fractionated, analyzed and used for further processing.

1. M-SERIES GUARDCASE HYDROTREATING

SUMMARY

Raffinates of distillate in situ shale oil were hydrotreated at mild conditions to prepare samples for freeze point modification via reforming. The initial mild hydrotreating did not make specification (<1 ppm sulfur and nitrogen) reformer feed. Rehydrotreating the materials at

higher severity produced specification feed. This rehydro-treating requirement was later found to have been caused by contamination of the raffinate.

OBJECTIVES

One objective of these tests was to determine stabilized activity of the catalyst for reducing sulfur, nitrogen and freeze point of pre-jet fuel streams. The second objective was to treat sufficient quantities of shale oil samples for fractionation, reforming and aromatic saturation processing.

MECHANICAL DESCRIPTION

The equipment used as the guardcase hydrotreater is shown in Figure VII-1. The reactor is 1" I.D., made of stainless steel and 49" long. Liquid is charged to the reactor by a Lapp diaphragm pump and hydrogen flow is controlled with a Brooks electric valve. Needle valves and a rotameter are used for backup manual control of hydrogen flow. Hydrogen sulfide is piped to the unit for catalyst sulfiding and nitrogen is provided for purging and pressure testing. Four controllers adjust electrical heating of the four reactor zones.

A small heat exchanger cools reactor effluent and a Grove backpressure regulator controls system pressure while letting down product to nearly atmospheric pressure. Products are scrubbed of H_2S by caustic in a downflow tube. The product stream then flows successively into a liquid

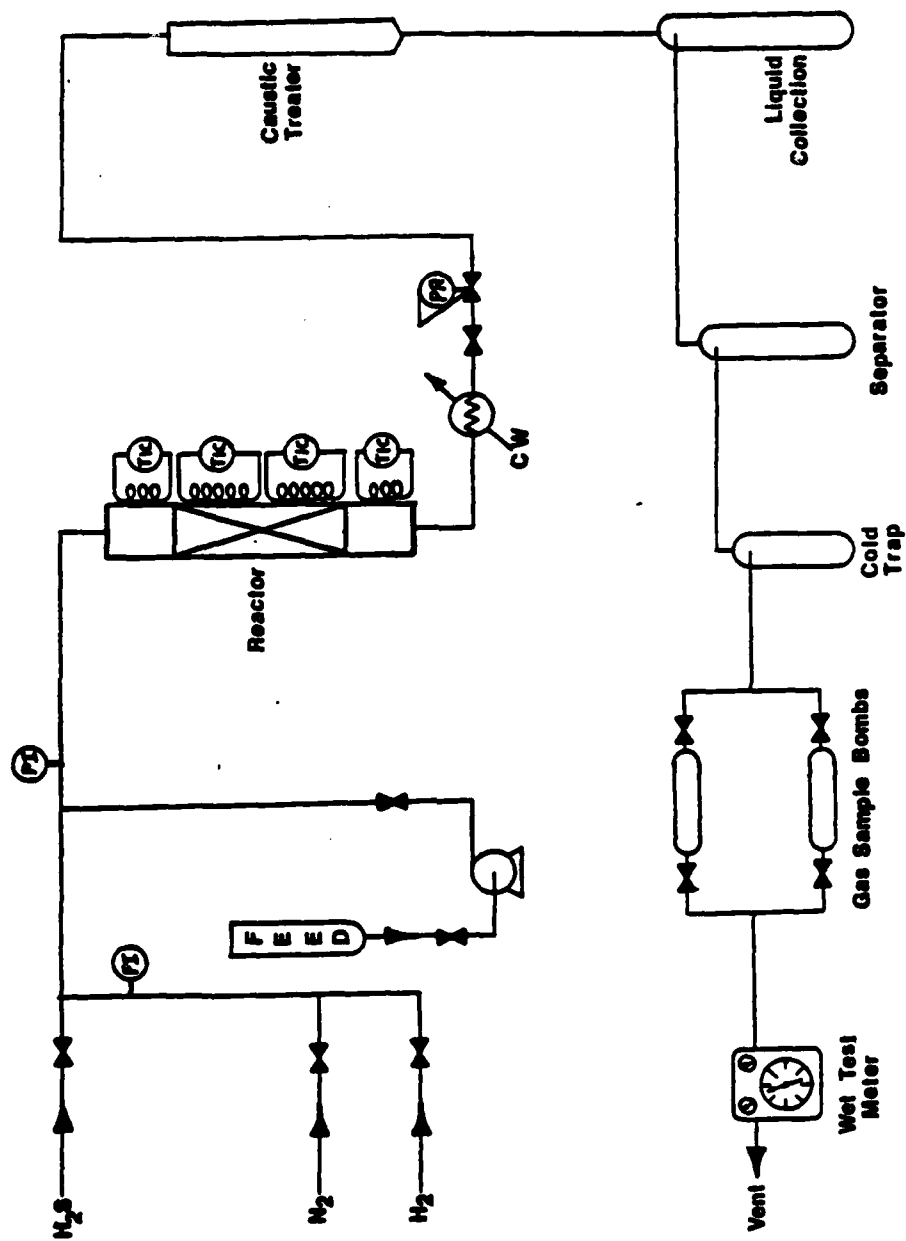


Figure VII-1. Guardcase Hydrotreater Configuration

product collector, a mist separator, a cold trap and gas sample bombs. Gases from the gas sample bombs pass through a water scrubber and a wet test meter before venting to the atmosphere.

CHEMICAL AND CATALYST DESCRIPTIONS

Feedstocks to these runs were prepared as described in Section VI. Properties of initial and rehydrotreating feedstocks are shown in Tables VII-1 and VII-2, respectively.

TABLE VII-1

INITIAL HYDROTREATING

| <u>Feedstock</u> | <u>°API</u> | <u>% S Weight</u> | <u>% N Weight</u> |
|------------------|-------------|-----------------------|-----------------------|
| M-112 Raffinate | 39.2 | .12 | .24 |
| M-121 Raffinate | 39.0 | .07 | .225 |

The hydrogen used is 99.95+ percent pure grade; the hydrogen sulfide is CP grade; and the sodium hydroxide pellets are electrolytic grade 97.2 percent NaOH, 0.40 percent Na₂CO₃. The hydrotreating catalyst is a nickel molybdate on 1/16" extrudate support.

TABLE VII-2
REHYDROTREATING

| <u>Feedstock</u> | <u>°API</u> | <u>S</u> | <u>N</u> |
|------------------------------------|-------------|----------|----------|
| M-112 Remixed Product Fractions | 41.5 | 13 ppm | 117 ppm |
| M-121 Remixed Product Fractions | 41.9 | 20 ppm | 72 ppm |

Other chemicals and catalysts were the same as the original runs.

EXPERIMENTAL PROCEDURE

The reactors for initial guardcase hydrotreating of M-112 and M-121 samples were packed with 50cc of 1/16" Ni/Mo catalyst and diluted with an equal volume of Ottawa sand in 10-ml increments. Postheat and preheat zones both were filled with tabular alumina.

For the rehydrotreating runs of M-112 and M-121, the reactors were packed with 250-ml of catalyst and sand each in alternate 10-ml increments. Postheat and preheat were again filled with tabular alumina.

The reactor system was purged with nitrogen and pressure tested with nitrogen and hydrogen successively to 200 psig above run pressure. The catalyst was presulfided by passing hydrogen sulfide through the reactor at 20 psig. Bed temperature was started at 200°F and increased 50°F every half-hour until attaining 50°F greater than the highest run temperature. The unit was blocked in for two hours

at final sulfiding temperature and full H₂S bottle pressure. The reactor was allowed to cool to 400°F and purged for ten minutes.

Catalyst break-in was accomplished as follows:

1. Begin H₂ flow to cold reactor at the specified rate
2. Set temperature controls to 300°F
3. Begin oil flow to reactor at the specified rate
4. Hold at 300°F for one hour, then raise temperatures to 400°F
5. Hold at 400°F for 30 minutes, then raise to 450°F
6. Thereafter raise temperature to final temperature in 50°F increments every 30 minutes

The first 12 hours of operation were break-in and lineout. Break-in and lineout materials were saved. Each run continued until the feed was nearly exhausted (50-ml left), then the break-in and lineout products were added to the feed reservoir and run until this feed was also exhausted.

The target run conditions for initial hydrotreating of both samples were:

2 LHSV (100cc/hr)
3000 SCFB H₂ (1.88 SCFH)
675°F
1000 psig
50cc of Ni/Mo 1/16" catalyst

The target conditions for rehydrotreating were:

1 LHSV (250cc/hr)

3000 SCFB H₂ (4.72 SCFH)

700°F

1200 psig

250cc of Ni/Mo 1/16" catalyst

Reactor effluent was cooled and scrubbed by in-line caustic pellets to remove dissolved H₂S from the liquid. The collected liquid was water-washed three times in a separatory funnel with equal volumes of deionized water to remove traces of caustic and ammonia. All liquid products were also stabilized at total reflux for two hours at 300°F pot temperature on an Oldershaw column.

EXPERIMENTAL RESULTS

INITIAL HYDROTREATING

The results for initial hydrotreating of M-112 and M-121 are presented in Tables VII-3 and VII-5. Table VII-3 displays the M-112 material balances and heteroatom contents. Table VII-5 displays similar data for M-121 initial hydrotreating products.

TABLE VII-3

**INITIAL GUARDCASE HYDROTREATING
SAMPLE M-112**

| Period | 1 | 2 | 3 | Total |
|-----------------------------|--------|--------|--------|-------|
| OPERATING CONDITIONS | | | | |
| Temperature, °F | 675 | 675 | 675 | |
| Pressure, PSIG | 1015 | 1011 | 1013 | |
| LHSV, Hr ⁻¹ | 1.93 | 1.97 | 1.80 | |
| H ₂ Rate, SCFB | 3109 | 3038 | 3389 | |
| MATERIAL BALANCE | | | | |
| Weight Percent of Feed | | | | |
| Feed | 100.00 | 100.00 | 100.00 | |
| H ₂ In | 5.66 | 5.53 | 6.17 | |
| Subtotal In | 105.66 | 105.53 | 106.17 | |
| H ₂ O | - | - | - | |
| NH ₃ | 0.28 | 0.26 | 0.03 | |
| H ₂ S | 0.09 | 0.09 | 0.01 | |
| H ₂ Out | 5.44 | 5.28 | 5.93 | |
| C ₁ | 0.13 | - | - | |
| C ₂ | 0.07 | 0.42 | 0.27 | |
| C ₃ | 0.11 | 0.37 | 1.05 | |
| C ₄ | 0.12 | 0.39 | 1.02 | |
| C ₅ | 0.16 | 0.41 | 0.70 | |
| Stabilized Liquid | 91.80 | 99.43 | 109.59 | |
| Subtotal | 98.20 | 106.65 | 118.6 | |
| Closure | 92.9 | 101.1 | 111.7 | |
| Hydrogen Consumption, SCFB | 121 | 137 | 132 | |
| PRODUCT PROPERTIES | | | | |
| °API | 41.9 | 41.6 | 42.0 | |
| Sulfur, ppm | 39 | 16 | 9 | |
| Nitrogen, ppm | 111 | 223 | 62 | |
| Oxygen, ppm | - | - | - | |

TABLE VII-4

**REHYDROTREATING OF SAMPLE M-112
THROUGH GUARDCASE HYDROTREATER**

| Period | 1 | 2 | 3 | 4 | Total |
|-----------------------------|--------|--------|--------|--------|-------|
| OPERATING CONDITIONS | | | | | |
| Temperature, °F | 706 | 706 | 706 | 705 | |
| Pressure, PSIG | 1212 | 1212 | 1212 | 1212 | |
| LHSV, Hr ⁻¹ | .87 | .98 | .99 | .65 | |
| H ₂ Rate, SCFB | 3434 | 3063 | 3028 | 4632 | |
| MATERIAL BALANCE | | | | | |
| Weight Percent of Feed | | | | | |
| Feed | 100.00 | 100.00 | 100.00 | 100.00 | |
| H ₂ In | 6.33 | 5.64 | 5.58 | 8.64 | |
| Subtotal In | 106.33 | 105.64 | 105.58 | 108.64 | |
| H ₂ O | - | - | - | - | |
| NH ₃ | 0.01 | 0.01 | 0.01 | 0.00 | |
| H ₂ S | 0.00 | 0.00 | 0.00 | 0.00 | |
| H ₂ Out | 3.11 | 5.01 | 5.14 | 7.96 | |
| C ₁ | 0.07 | 0.11 | 0.11 | 0.17 | |
| C ₂ | 0.04 | 0.07 | 0.07 | 0.11 | |
| C ₃ | 0.09 | 0.15 | 0.15 | 0.23 | |
| C ₄ | 0.10 | 0.16 | 0.17 | 0.26 | |
| C ₅ | 0.06 | 0.08 | 0.09 | 0.14 | |
| Stabilized Liquid | 101.66 | 93.93 | 117.55 | 97.52 | |
| Subtotal | 105.14 | 99.53 | 123.30 | 106.41 | |
| Closure | 98.88 | 94.21 | 116.79 | 97.94 | |
| Hydrogen Consumption, SCFB | 1743 | 343 | 237 | 364 | |
| PRODUCT PROPERTIES | | | | | |
| °API | 45.5 | 44.4 | 44.0 | 45.0 | |
| Sulfur, ppm | 2 | 1 | 1 | 1 | |
| Nitrogen, ppm | 1 | 1 | 1 | 1 | |
| Oxygen, Wt % | | | | | |

TABLE VII-5

INITIAL GUARDCASE HYDROTREATING

SAMPLE M-121

| Period | 1 | 2 | 3 | 4 |
|----------------------------|--------|--------|--------|--------|
| OPERATING CONDITIONS | | | | |
| Temperature, °F | 679 | 674 | 674 | 672 |
| Pressure, PSIG | 999 | 1000 | 1000 | 1000 |
| LHSV, Hr ⁻¹ | 2.02 | 2.04 | 2.04 | 1.97 |
| H ₂ Rate, SCFB | 3120 | 3025 | 3096 | 3046 |
| MATERIAL BALANCE | | | | |
| Weight Percent of Feed | | | | |
| Feed | 100.00 | 100.00 | 100.00 | 100.00 |
| H ₂ In | 5.71 | 5.54 | 5.66 | 5.57 |
| Subtotal In | 105.71 | 105.54 | 105.66 | 105.57 |
| H ₂ O | - | - | - | - |
| NH ₃ | .27 | .26 | .25 | - |
| H ₂ S | .07 | .07 | .07 | - |
| H ₂ Out | 4.77 | 5.12 | 4.97 | 5.56 |
| C ₁ | .07 | 0.25 | - | 0.03 |
| C ₂ | .05 | 0.17 | 0.63 | 0.03 |
| C ₃ | .12 | 0.44 | 1.28 | 0.06 |
| C ₄ | .05 | 0.14 | 0.19 | 0.03 |
| C ₅ | .11 | 0.36 | 0.22 | 0.02 |
| Stabilized Liquid | 99.83 | 96.85 | 98.10 | 101.27 |
| Subtotal | 105.07 | 103.67 | 105.71 | 107.00 |
| Closure | 99.4 | 98.2 | 100.05 | 101.4 |
| Hydrogen Consumption, SCFB | 514 | 228 | 380 | 7 |
| PRODUCT PROPERTIES | | | | |
| °API | 42.1 | 42.6 | 42.1 | 41.9 |
| Sulfur, ppm | 33 | 36 | 32 | 34 |
| Nitrogen, ppm | 21 | 122 | 166 | 24 |
| Oxygen, ppm | - | - | - | - |

REHYDROTREATING

The results for rehydrotreatment of M-112 and M-121 are presented in Tables VII-4 and VII-6. The M-112 retreat feed contained 13 ppm sulfur and 117 ppm nitrogen, with an API Gravity of 41.5°. The M-121 retreat feed contained 20 ppm sulfur and 72 ppm nitrogen, with an API gravity of 41.9°. Table VII-4 shows the material balances for the rehydrotreating of M-112, while Table VII-6 shows the material balances for the rehydrotreating of M-121.

The M-112 product at 44.8°API was fractionated into IBP-520°F (1565gr and 48.1°API) and 520°F+ (523gr and 42.7°API) cuts before reforming; the 520°F+ diesel stream was not further processed. The M-121 product at 45.3°API was not fractionated before reforming.

DISCUSSION OF RESULTS

INITIAL HYDROTREATING

The only major problem encountered during these runs was a water-soluble precipitate which formed in the unit feed buret. The precipitate was found to be unremoved extraction compounds. Results from these runs are somewhat unexpected in that: (1) high heteroatom concentrations in the product were encountered and (2) apparent extreme catalyst deactivation was observed. The deactivation was most probably due to the aforementioned sample contamination.

TABLE VII-6

**REHYDROTREATING OF SAMPLE M-121
THROUGH GUARDCASE HYDROTREATER**

| Period | 1 | 2 | 3 | 4 | 5 | Total |
|-----------------------------|--------|--------|--------|--------|--------|-------|
| OPERATING CONDITIONS | | | | | | |
| Temperature, °F | 706 | 703 | 701 | 702 | 700 | |
| Pressure, PSIG | 1218 | 1218 | 1216 | 1218 | 1218 | |
| LHSV, Hr ⁻¹ | 0.99 | 0.99 | 1.00 | 1.00 | 0.77 | |
| H ₂ Rate, SCFB | 3036 | 3033 | 2996 | 2996 | 3107 | |
| MATERIAL BALANCE | | | | | | |
| Weight Percent of Feed | | | | | | |
| Feed | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | |
| H ₂ In | 5.61 | 5.60 | 5.53 | 5.53 | 5.85 | |
| Subtotal In | 105.61 | 105.60 | 105.53 | 105.53 | 105.85 | |
| H ₂ O | - | - | - | - | - | |
| NH ₃ | 0.01 | 0.01 | 0.01 | 0.01 | 0.00 | |
| H ₂ S | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | |
| H ₂ Out | 4.48 | 4.47 | 4.27 | 4.34 | 4.96 | |
| C ₁ | 0.09 | 0.09 | 0.08 | 0.08 | 0.10 | |
| C ₂ | 0.15 | 0.15 | 0.14 | 0.15 | 0.17 | |
| C ₃ | 0.39 | 0.39 | 0.38 | 0.38 | 0.43 | |
| C ₄ | 0.25 | 0.25 | 0.24 | 0.24 | 0.27 | |
| C ₅ | 0.16 | 0.16 | 0.16 | 0.16 | 0.18 | |
| Stabilized Liquid | 97.15 | 94.09 | 96.33 | 102.68 | 115.87 | |
| Subtotal | 102.67 | 99.61 | 101.59 | 108.05 | 121.99 | |
| Closure | 97.23 | 94.33 | 96.27 | 102.39 | 115.25 | |
| Hydrogen Consumption, SCFB | 607 | 613 | 687 | 643 | 473 | |
| PRODUCT PROPERTIES | | | | | | |
| °API | 45.2 | 45.2 | 44.8 | 44.6 | 45.9 | |
| Sulfur, ppm | 1 | 1 | 1 | 1 | 1 | |
| Nitrogen, ppm | 1 | 1 | 1 | 1 | 1 | |
| Oxygen, ppm | - | - | - | - | - | |

Since the sulfur and nitrogen contents of the products were greater than 1 ppm, two further runs were made to rehydrotreat the M-112 and M-121 samples.

REHYDROTREATING

Rehydrotreating the M-112 and M-121 samples achieved the objective of reducing the sulfur and nitrogen contents to <1 ppm.

A JP-4 fraction and a diesel fraction were made from the M-112 sample, while the M-121 sample became a JP-8 turbine fuel.

The freeze points of the JP-4 fraction of M-112 and the JP-8 fraction of M-121 both were not yet low enough to meet jet fuel specifications of -72°F for a JP-4 fuel and -58°F for a JP-8 fuel. The M-112 JP-4 fraction had a -56°F freeze point and the M-121 JP-8 fraction had a -33.7°F freeze point.

CONCLUSIONS

- The tested M-112 and M-121 materials were slightly contaminated with unremoved extraction compounds.
- The contaminated M-112 and M-121 materials rapidly deactivated the Ni/Mo hydrotreating catalyst at mild conditions.
- The contaminated M-112 and M-121 material were successfully rehydrotreated to <1 ppm sulfur and nitrogen.

- It is recommended that additional cleanup steps be provided between extraction and guardcase hydrotreating.
- The freeze points of the JP-4 and JP-8 guardcase hydrotreated fractions do not meet turbine fuel specifications.

2. GUARDCASE HYDROTREATING

SUMMARY

The most important aspect of the GC-1 test was to define the required guardcase severity for in situ raffinate. Since the M-Series raffinate had been contaminated with unremoved extraction compounds the GC-series raffinates were processed under additional cleanup steps. The GC-1 tests confirmed that an uncontaminated shale oil raffinate can easily be upgraded to reformat feed specifications. The GC-1 catalyst showed no apparent deactivation.

The GC-1 products were separated into two categories: (1) main portion "ON SPEC" material for further processing and final samples, (2) pseudocomponent fractionation stocks. Various pseudocomponents were analyzed for °API, Reid vapor pressure, simulated distillation, viscosity, FIA and freeze point. The pseudocomponent analyses allowed calculation of fractionation and blending to make JP-4, JP-5, JP-8, diesel and gasoline samples from the fully processed GC-1 sample.

OBJECTIVES

There are four objectives of the GC-1 guardcase hydrotreating tests:

1. Determine the least severe operating conditions required for guardcase hydrotreating to <1 ppm nitrogen and sulfur.
2. Operate the reactor for several days at conditions that achieve <1 ppm nitrogen and sulfur.
3. Treat enough shale oil product to use in later freeze point modification tests and pseudocomponent distillations.
4. Determine whether extracted shale oil that is not contaminated can be hydrotreated less severely to specification than the contaminated M-Series shale oils.

MECHANICAL DESCRIPTION

Figure VII-1 shows the reactor scheme used for GC-1 hydrotreating. The scheme is the same as described for the M-Series guardcase hydrotreater.

CHEMICAL AND CATALYST DESCRIPTION

Feedstock for this study was prepared as described in Section V for samples OXY-1, OXY-2, OXY-3 and OXY-4. These raffinates were blended, resulting in the properties shown below:

| | <u>S</u> | <u>N</u> | <u>°API</u> |
|--|----------|----------|-------------|
| Blend of Occidental Shale Oil Raffinates for #1, #2, #3 and #4 | .0634% | .20% | 38.2° |

The hydrogen used in the guardcase hydrotreater was 99.95+ percent pure; the hydrogen sulfide was CP grade from Linde; the sodium hydroxide was electrolytic pellet 97.2 percent NaOH and 0.40 percent Na₂CO₂; and the catalyst was nickel molybdate on 1/16" support.

DESCRIPTION OF EXPERIMENTAL PROCEDURE

The GC-1 study used a reactor packed with 80cc of 1/16" Ni/Mo catalyst diluted with 160-ml of Ottawa sand in 20-ml increments. Postheat and preheat zones were filled with tabular alumina.

The units were purged with nitrogen, pressure tested first with nitrogen, then hydrogen to 200 psig greater than run pressure. Sulfiding the catalyst was accomplished by passing hydrogen sulfide through the reactor at 20 psig. The bed temperature was started at 200°F and increased 50°F every half-hour until attaining 50°F greater than the highest run temperature. The unit was blocked-in for two hours at the final sulfiding temperature and full H₂S bottle pressure. After the two hours blocking, the reactor was allowed to cool to 400°F and purged with nitrogen for ten minutes.

Catalyst break-in was performed as follows:

1. Set H₂ flow to cold reactor at 1.88 SCF/Hr
2. Set temperature controls to 300°F
3. Set oil flow to reactor at 100cc/hr
4. Held at 300°F for one hour, then raised temperatures to 400°F
5. Held at 400°F for thirty minutes, then raised to 450°F
6. Thereafter raised temperature to 675°F in 50°F increments every thirty minutes

The first 18 hours of operation were break-in and lineout. Break-in and lineout material were saved. The run continued until the original feed nearly ran out. The break-in and some off-spec product were then recycled to the feed reservoir and run until the feed was exhausted.

The conditions for GC-1 were as follows:

| | | | | |
|--------|-------|----------------------|-----------|---|
| Test 1 | 650°F | 1 LHSV (80 ml/hr) | 800 psig | 4000 SCFB H ₂ (2.01 SCFH) |
| Test 2 | 650°F | 1 LHSV (80 ml/hr) | 1000 psig | 4000 SCFB H ₂ (2.01 SCFH) |
| Test 3 | 650°F | 1 LHSV (80 ml/hr) | 1200 psig | 4000 SCFB H ₂ (2.01 SCFH) |
| Test 4 | 675°F | 1 LHSV (80 ml/hr) | 1200 psig | 4000 SCFB H ₂ (2.01 SCFH) |
| Test 5 | 700°F | 1 LHSV (80 ml/hr) | 1200 psig | 4000 SCFB H ₂ (2.01 SCFH) |

Since the reactor products were scrubbed by caustic to remove dissolved H₂S from the liquid, the liquid collected was water-washed at least three times in a separatory

funnel with an equal volume of fresh deionized water. As an added precaution against leftover contamination from dissolved NH_3 and H_2S , all liquid products were stabilized at total reflux for two hours at 300°F pot temperature on an Oldershaw fractionation column.

EXPERIMENTAL RESULTS

The experimental results of GC-1 are presented in Table VII-7.

Four pseudocomponent distillations were performed on GC-1 materials. The distilled materials were:

- GC-1 feed
- Lineout #1 product
- Lineout (L.O.) #2 + L.O. #3 + L.O. #4 + L.O. #5 + Test #1 product
- Test #2 + Test #3 + Test #4 + all periods from Test #5 ("ON SPEC")

Each of the four groups has different sulfur and nitrogen contents. The pseudocomponent boiling ranges were IBP-290°F, 290-400°F, 400-510°F, 510-570°F and 570°F+. A Todd fractionation column operated at 5:1 reflux was used to fractionate the material. Tables VII-8 through VII-11 display the pseudocomponent properties.

The main portion of "ON SPEC" product was later used for freeze point modification processing.

TABLE VII-7

GUARDCASE HYDROTREATING OF SAMPLE GC-1

| Period | 1 | 2 | 3 | 4 | 5.1 | 5.2 | 5.3 | 5.4 |
|----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| OPERATING CONDITIONS | | | | | | | | |
| Temperature, °F | 651 | 650 | 649 | 675 | 700 | 700 | 700 | 699 |
| Pressure, PSIG | 813 | 1010 | 1217 | 1210 | 1209 | 1212 | 1201 | 1185 |
| LHSV, Hr ⁻¹ | 1.00 | 1.02 | 0.98 | 0.95 | 0.98 | 0.95 | 0.98 | 0.92 |
| Hydrogen Rate, SCFB | 3979 | 3925 | 4086 | 4215 | 4070 | 4193 | 4086 | 4341 |
| MATERIAL BALANCE | | | | | | | | |
| Weight Percent of Feed | | | | | | | | |
| Feed | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| Hydrogen In | 7.19 | 7.10 | 7.39 | 7.61 | 7.36 | 7.58 | 7.39 | 7.85 |
| Subtotal In | 107.19 | 107.10 | 107.39 | 107.61 | 107.36 | 107.58 | 107.39 | 107.85 |
| H ₂ O | - | - | - | - | - | - | - | - |
| H ₂ S | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 |
| NH ₃ | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 | 0.24 |
| Hydrogen Out | 6.48 | 6.17 | 5.68 | 6.77 | 6.27 | 6.31 | 6.45 | 5.68 |
| C ₁ | 0.00 | 0.00 | 0.00 | 0.16 | 0.41 | 0.00 | 0.00 | 0.00 |
| C ₂ | 0.30 | 0.56 | 0.30 | 0.08 | 0.35 | 0.47 | 0.69 | 0.61 |
| C ₃ | 0.56 | 0.82 | 0.39 | 0.11 | 0.44 | 0.62 | 2.54 | 2.24 |
| C ₄ | 0.27 | 0.43 | 0.39 | 0.10 | 0.35 | 0.57 | 0.63 | 0.56 |
| C ₅ | 0.96 | 0.58 | 1.00 | 0.29 | 0.63 | 0.85 | 0.96 | 0.84 |
| Stabilized Liquid | 101.60 | 103.33 | 104.25 | 97.48 | 103.05 | 104.32 | 97.95 | 102.88 |
| Subtotal Out, %wt | 110.49 | 112.20 | 112.33 | 105.31 | 111.84 | 113.46 | 109.55 | 113.15 |
| Closure, %wt | 103.07 | 104.76 | 104.61 | 97.85 | 104.17 | 107.58 | 102.02 | 104.91 |
| oAPI | 41.5 | 41.9 | 41.7 | 42.2 | 42.9 | 42.8 | 42.6 | 42.6 |
| Sulfur, ppm | 1.8 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Nitrogen, ppm | 5.8 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Basic Nitrogen, %wt | - | - | - | - | - | - | - | - |
| Hydrogen Consumption, SCFB | 393 | 513 | 943 | 468 | 601 | 700 | 518 | 1196 |

TABLE VII-8

TODD PSEUDOCOMPONENTS

GC-1 FEED

| | IBP-290°F | 290-400°F | 400-510°F | 510-570°F | 570+°F |
|--------------------------|-----------|--------------|--------------|--------------|--------|
| Wt% yield | 11.05 | 21.75 | 41.66 | 22.95 | 2.58 |
| °API | 53.6 | 42.9 | 36.1 | 31.9 | - |
| RVP | - | 0.4 lb | 0.2 lb | - | - |
| Vis 100°F (cst) 210°F | - | 1.03 0.71 | 1.97 0.99 | 3.59 1.36 | - |
| FREEZE, °F | -90 | -90 | -40 | +6.8 | - |
| FIA Saturates | - | - | - | - | - |
| Olefins | - | - | - | - | - |
| Aromatics | - | - | - | - | - |
| SM-D IBP D-2887 | 101°F | 250°F | 357°F | 469°F | 395°F |
| 2% | 133 | 267 | 376 | 482 | 536 |
| 10% | 174 | 291 | 404 | 504 | 561 |
| 50% | 254 | 347 | 459 | 547 | 590 |
| 90% | 323 | 399 | 516 | 578 | 730 |
| 98% | 358 | 425 | 543 | 590 | 861 |
| EP | 484 | 445 | 561 | 620 | 907 |

TABLE VII-9

TODD PSEUDOCOMPONENTS

GC-1 LINEOUT 1

| | IBP-290°F | 290-400°F | 400-510°F | 510-570°F | 570+°F |
|---------------------------|-----------|--------------|--------------|--------------|--------|
| Wt% yield | 8.86 | 24.62 | 46.01 | 16.57 | 3.93 |
| °API | 57.4 | 45.0 | 37.9 | 37.2 | 37.4 |
| RVP | - | 0.35 lb | 0.25 lb | - | - |
| Vis 100 °F (cst) 210°F | - | 0.94 0.55 | 1.93 0.91 | 3.64 1.35 | - |
| FREEZE, °F | - | -90 | -41.8 | - | - |
| FIA Saturates | 82.2 | 68.5 | 58.3 | - | - |
| Olefins | 1.3 | 1.7 | 8.0 | - | - |
| Aromatics | 16.5 | 29.8 | 33.0 | - | - |
| SM-O IBP D-2887 | 133°F | 229°F | 370°F | 500 °F | 556 °F |
| 2% | 144 | 252 | 384 | 505 | 560 |
| 10% | 193 | 286 | 408 | 517 | 571 |
| 50% | 249 | 345 | 458 | 546 | 591 |
| 90% | 302 | 394 | 507 | 574 | 751 |
| 98% | 333 | 418 | 521 | 584 | 760 |
| EP | 352 | 441 | 538 | 607 | 818 |

TABLE VII-10

TODD PSEUDOCOMPONENTS

GC-1 LINEOUT 2,3,4,5,& TEST 1

| | BP-290°F | 290-400°F | 400-510°F | 510-570°F | 570+°F |
|--------------------------|----------|--------------|--------------|--------------|--------------|
| Wt% yield | 15.65 | 14.44 | 44.02 | 23.84 | 2.06 |
| °API | 55.6 | 43.8 | 38.9 | 38.4 | 35.8 |
| RVP | 1.75 lb | 0.05 lb | 0.05 lb | - | - |
| Vis 100°F (cst) 210°F | - | 0.99 0.57 | 1.75 0.86 | 3.45 1.31 | 8.48 2.39 |
| FREEZE, °F | -90 | -90 | -48.1 | +6.8 | - |
| FIA Saturates | 82.6 | 68.8 | 67.5 | 76.4 | - |
| Olefins | 0.8 | 1.0 | 1.6 | 8.0 | - |
| Aromatics | 16.6 | 30.2 | 30.9 | 15.6 | - |
| SM-D BP D-2887 | 95°F | 295°F | 342°F | 475°F | 499°F |
| 2% | 140 | 311 | 356 | 484 | 530 |
| 10% | 194 | 325 | 385 | 505 | 572 |
| 50% | 272 | 351 | 447 | 541 | 597 |
| 90% | 314 | 396 | 495 | 579 | 754 |
| 98% | 355 | 439 | 513 | 588 | 818 |
| EP | 445 | 466 | 521 | 598 | 867 |

TABLE VII-11

TODD PSEUDOCOMPONENTS

GC-1 ONSPEC

| | 1BP-290°F | 290-400°F | 400-510°F | 510-570°F | 570+°F |
|--------------------------|--------------|--------------|--------------|--------------|--------|
| Wt% yield | 15.33 | 25.61 | 37.58 | 15.40 | 6.08 |
| °API | 56.6 | 44.3 | 38.8 | 38.6 | 40.3 |
| RVP | 1.9 lb | 0.5 lb | 0.0 lb | - | - |
| Vis 100°F (cst) 210°F | 1.02 0.61 | 1.99 0.93 | 3.22 1.24 | 5.37 1.83 | - |
| FREEZE, °F | -90 | -90 | -40 | +10.3 | +29.3 |
| FIA Saturates | 83.8 | 73.7 | 73.5 | 81.2 | - |
| Olefins | 1.1 | 1.0 | 1.4 | 2.3 | - |
| Aromatics | 15.1 | 25.3 | 25.1 | 16.5 | - |
| SM-O IBP D-2887 | 97°F | 245°F | 389°F | 447°F | 520°F |
| 2% | 140 | 271 | 401 | 476 | 552 |
| 10% | 193 | 300 | 419 | 493 | 567 |
| 50% | 259 | 357 | 457 | 529 | 586 |
| 90% | 311 | 400 | 505 | 563 | 606 |
| 98% | 343 | 415 | 523 | 575 | 729 |
| EP | 381 | 427 | 544 | 583 | 759 |

DISCUSSION OF RESULTS

All objectives of the run were met. Most important, under relatively mild conditions of Test #2, the shale oil raffinate was successfully treated to <1 ppm nitrogen and sulfur. Thus contaminant-free raffinate hydrotreats much easier than did the raffinate from the M-Series runs.

It was planned to stop increasing reactor severity when the product nitrogen and sulfur levels reached <1 ppm, but data turnaround was such that the minimum severity required was exceeded inadvertently.

CONCLUSIONS

All four objectives for the run were met.

- The least severe conditions for hydrotreating GC-1 shale oil raffinate to <1 ppm sulfur and nitrogen were 650°F; 1 LHSV and 1000 psig at 4000 SCFB hydrogen circulation.
- The reactor was operated at constant conditions for 3-1/2 days and operated for over 6-1/2 days during the run.
- Sufficient "ON SPEC" GC-1 shale oil was prepared for later processing tests and final samples.
- The uncontaminated shale oil raffinate was successfully hydrotreated to <1 ppm sulfur and nitrogen at a much lower severity than the contaminated M-Series raffinates required.

SECTION VIII
FREEZE POINT MODIFICATION

Yet another unique application of the EXTRACTACRACKING process is the ability to selectively modify the freeze point of shale oil derived jet fuels. While freeze point can be attained in some cases by distillation corrections, modification of the freeze point allows an increased yield of jet fuel under otherwise constant conditions.

Studies performed during Phase II encompassed a simulated prescreening, processing of two M-Series samples at conditions defined by the prescreening, and an accelerated aging run to determine if the high endpoint feedstock would cause excessive catalyst deactivation.

Products from these studies were fractionated into appropriate boiling ranges and the targeted jet fuel products supplied to aromatic saturation.

1. SIMULATION OF FREEZE POINT MODIFICATION BY BLENDS OF JET FUEL AND NORMAL PARAFFINS

SUMMARY

Studies were performed to demonstrate the effectiveness of freeze point modification on normal paraffins and normal paraffin-doped jet fuels. Experimentation was performed on cetane (n-hexadecane) for scoping purposes; parameter variation studies provided for a JP-7 fuel doped with 10 percent dodecane, 10 percent tetradecane and 10

percent hexadecane; and finally both reforming and aromatic saturation were carried out with intermediate and final distillation analysis of the doped JP-7 feedstocks. Freeze point depressions up to 100°F were accomplished and a series of correlative curves developed.

OBJECTIVES

The purpose of this work was threefold: (1) determine the effectiveness of Ashland's freeze point modification process, (2) determine freeze point, product property and product yield response to process parameters, and (3) determine the interactions between freeze point modification and aromatic saturation for JP-4 and JP-8 fractions.

EQUIPMENT AND EXPERIMENTAL

These experiments were performed in a 316 stainless steel 1" I.D. Universal reactor heated by a radiant heat furnace. The temperatures were controlled through the use of Thermo Electric Selectrol switches and measured by means of a Honeywell temperature indicator and Iron-Constantan thermocouples located throughout the reactor (preheat, catalyst bed, postheat). The feed was metered from a capped (air bleed equalizer) graduate via a Lapp pump. The hydrogen was metered to the reactor through a Brooks continuous flow electronic equalizer. The effluent gas was separated from the liquid product in a Jerguson liquid level gauge and depressured to atmospheric pressure through a Grove

pressure regulator. The effluent gas and any light gases from the liquid (after discharging to atmospheric pressure in a closed system) were passed through two acetone-dry ice traps and then measured by means of a wet test meter. The material collected in the dry ice traps and the liquid product were combined and stabilized to a 5°C overhead to yield a C₅+ reformat. Spot gas samples were taken during various periods of the test cycle, submitted for gas chromatographic analysis and the values averaged and normalized to yield a light gas value for each experiment.

The catalyst utilized in this test series was a bi-metallic extrudate containing platinum and rhenium on a chlorided alumina. The catalyst was charged to the reactor in a pseudo-logarithmic bed configuration employing six bed sections (catalyst plus 35-ml of tabular alumina) with catalyst concentration increasing as one progresses from the top of the reactor to the bottom. The direction of hydrocarbon and gas flow was downflow. The catalyst was prereduced by treatment with flowing hydrogen (1-2 cu.ft. per hour), starting at room temperature and continuing up to and including operating temperature and pressure.

From this study and correlation, two sets of process conditions were picked to give the highest liquid yield, lowest freeze point and substantial aromatics in the product (greater than 20 weight percent). These two sets of conditions were picked so that extended runs could be made to obtain enough product to fractionate and yield JP-4 and

JP-8 jet fuel fractions for product properties evaluation (yield, freeze point, aromatic content). The JP-4 and JP-8 fractions were then hydrogenated to lower aromatic content and the effect on freeze point and the ease of hydrogenation were evaluated.

FEEDSTOCKS

Feedstock for the initial cetane study was laboratory grade n-hexadecane (cetane) measuring 98.8 percent saturates by FIA analysis. Properties are shown in Table VIII-1.

Feedstock for all remaining runs was doped JP-7, also shown in Table VIII-1.

RESULTS

The purpose of this study was to reform a n-paraffin containing petroleum based jet fuel (simulating a shale oil jet fuel fraction) under varying conditions of temperature, pressure and space velocity. This feedstock would have a high freeze point (off specifications), contain little or no aromatics which, upon reforming, would yield a total product meeting freeze point requirements and contain aromatics in the 20-40 weight percent range. Then through interpretation and correlation of this data, some insight could be gained into process conditions which would convert a high freeze point n-paraffin containing jet fuel to a low freeze point aromatic containing jet fuel. From this test series the best range of conditions that produced the improved jet fuel could be determined. Then an extended test

TABLE VIII-1

FREEZE POINT MODIFICATION SIMULATION - FEEDSTOCK PROPERTIES

| <u>DOPED</u> | | <u>CETANE</u> |
|-------------------------------|--------|---------------|
| 70% JP-7 | | |
| 10% Dodecane | | |
| 10% Tetradecane | | |
| 10% Hexadecane | | |
| FREEZE PT. °F = +9.5°F | | +68°F |
| S | - 97.1 | 98.8 |
| O | - 1.0 | 0.4 |
| A | - 1.9 | 0.08 |
| <u>SIM-D CUMULATIVE WT. %</u> | | |
| C5-130 | - 0 | 0 |
| 130-518 (JP4) | - 87 | 1.7 |
| 330-572 (JP8) | - 100 | 95.3 |
| 572+ | | 100.0 |
| IBP | 349 | 513 |
| 10 | 386 | 542 |
| 20 | 401 | - |
| 30 | 416 | 551 |
| 40 | 423 | - |
| 50 | 427 | 556 |
| 60 | 441 | - |
| 70 | 473 | 560 |
| 80 | 490 | - |
| 90 | 546 | 564 |
| 100 | 562 | 579 |

run could be made to produce sufficient quantity of product that would be fractionated to yield the JP-4 and JP-8 jet fuel fractions for more detailed analysis. Should one or more of the individual fractions not meet the freeze point specifications (although as total product they may have exceeded freeze point requirements), a study would follow of the hydrogenation of these fractions to convert the aromatics to naphthenes and to determine to what extent the freeze point had been lowered.

The process conditions and results of this study are given in the attached Tables VIII-2 through VIII-5 and Figures VIII-1 through VIII-13. The feedstock utilized in this reforming study was a JP-7 (-46°F freeze point, 2.5 weight percent aromatics) which contained 10 volume percent each of dodecane, tetradecane and hexadecane. The inclusion of 30 volume percent n-paraffins raised the freeze point to $+10^{\circ}\text{F}$, but had little effect on the distillation range of the original jet fuel. Tables VIII-3 through VIII-5 give the results obtained by reforming this feedstock at three different temperatures ($850, 880, 910^{\circ}\text{F}$), three different pressures (150, 250, 500 psig) and three different space velocities (2, 4, 8 LHSV). With the liquid product measured and all freeze points, aromatic contents, and SIM-D distillations reported, JP-4 and JP-8 yields and all weight balances were corrected to a 100 weight percent basis.

TABLE VIII-2

REFORMING OF CETANE

| RUN | 1 | 2 | 3 |
|-------------------------|------|------|------|
| <u>Conditions</u> | | | |
| Temp. °F | 750 | 825 | 900 |
| Pressure PSIG | 250 | 250 | 250 |
| LHSV | 8 | 8 | 8 |
| H ₂ /H C | 5/1 | 5/1 | 5/1 |
| <u>Product Analyses</u> | | | |
| Freeze Pt-°F | 51.8 | 27.5 | -8.5 |
| Saturates | 98.3 | 89.6 | 72.3 |
| Olefins | 0.4 | 1.4 | 1.9 |
| Aromatics | 1.3 | 9.0 | 25.8 |
| <u>SIM-D</u> | | | |
| IBP | 126 | 100 | 74 |
| 10 | 299 | 285 | 208 |
| 30 | 516 | 477 | 363 |
| 50 | 544 | 524 | 486 |
| 70 | 552 | 538 | 530 |
| 90 | 559 | 552 | 556 |
| EP | 568 | 613 | 667 |
| Liquid Recovery | 99.4 | 95.8 | 85.3 |
| Wt.% Feed | | | |

TABLE VIII-3

REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL

| <u>RUN</u> | <u>66-1</u> | <u>66-2</u> | <u>67-1</u> | <u>67-2</u> |
|--|-------------|-------------|-------------|-------------|
| Catalyst - Gms. | 35 | → | 35 | → |
| <u>Conditions</u> | | | | |
| Temp. °F | 850 | 910 | 880 | 910 |
| Pressure-PSIG | 150 | 150 | 150 | 150 |
| LHSV | 8 | → | → | 4 |
| H ₂ /H C | 5/1 | → | → | → |
| <u>Liq. Prod. Analysis</u> | | | | |
| Freeze Pt (°F) | -46 | -71 | -82 | -90 |
| S | 67.0 | 53.6 | 42.6 | 48.1 |
| O | 2.6 | 4.0 | 6.8 | 1.9 |
| A | 30.4 | 42.4 | 50.6 | 50.0 |
| <u>SIM-D-Wt. %</u> | | | | |
| C ₅ -I ₃₀ | 1.7 | 6 | 3 | 5 |
| 130-518 (JP4) | 89 | 83.0 | 86 | 83 |
| 330-572 (JP8) | 89 | 72 | 76 | 70 |
| 572+ | 2.0 | 3 | 3 | 4 |
| <u>Wt. Balance</u> | | | | |
| H ₂ +C ₁ +C ₂ | 3.20 | 3.88 | 4.70 | 5.98 |
| C ₃ +C ₄ | 4.73 | 7.30 | 7.91 | 8.69 |
| C ₅ + | 95.83 | 90.30 | 88.72 | 86.85 |
| Total | 103.76 | 101.48 | 101.33 | 101.52 |
| <u>Wt. Balance</u> | | | | |
| <u>Corrected to 100%</u> | | | | |
| H ₂ +C ₁ +C ₂ | 3.1 | 3.8 | 4.6 | 5.9 |
| C ₃ +C ₄ | 4.6 | 7.2 | 7.8 | 8.5 |
| C ₅ + | 95.3 | 89.0 | 87.6 | 85.6 |
| C ₅ +Vol. % Yield (100% Basis) | 95.2 | 90.8 | 81.0 | 89.0 |

TABLE VIII-4

REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL

| <u>RUN</u> | <u>60-1</u> | <u>60-2</u> | <u>61-1</u> | <u>61-2</u> | <u>62-1</u> | <u>62-2</u> |
|--|-------------|-------------|-------------|-------------|-------------|-------------|
| Catalyst - Gms. | 35 | → | 17.5 | → | 17.5 | → |
| <u>Conditions</u> | | | | | | |
| Temp. °F | 850 | 910 | 880 | 880 | 850 | 910 |
| Pressure-PSIG | 250 | 250 | 250 | 250 | 250 | 250 |
| LHSV | 2 | 2 | 4 | 8 | 8 | 8 |
| H ₂ /H C | 5.1 | | | | | |
| <u>Liq. Prod. Analysis</u> | | | | | | |
| Freeze Pt (°F) | -90 | -73 | -72 | -62 | -45 | -85 |
| S | 62.0 | 47.6 | 61.1 | 66.7 | 69.3 | 57.0 |
| O | 0.5 | 0 | 0.8 | 2.1 | 3.5 | 2.6 |
| A | 37.5 | 52.4 | 38.1 | 31.2 | 27.2 | 40.4 |
| <u>SIM-D-Wt. %</u> | | | | | | |
| C ₅ -130 | 4 | 9 | 5 | 3 | 0 | 5 |
| 130-518 (JP4) | 89 | 83 | 86 | 87 | 91 | 87 |
| 330-572 (JP8) | 69 | 58 | 71 | 82 | 88 | 71 |
| 572+ | 2 | 3 | 3 | 2 | 2 | 2 |
| <u>Wt. Balance</u> | | | | | | |
| H ₂ +C ₁ +C ₂ | 7.04 | 11.51 | 5.53 | 3.67 | 3.06 | 5.06 |
| C ₃ +C ₄ | 6.12 | 10.26 | 6.46 | 4.26 | 2.09 | 10.16 |
| C ₅ + | 87.23 | 79.06 | 88.03 | 91.68 | 94.23 | 85.06 |
| Total | 100.39 | 100.83 | 100.02 | 99.61 | 99.38 | 100.28 |
| <u>Wt. Balance Corrected to 100%</u> | | | | | | |
| H ₂ +C ₁ +C ₂ | 7.0 | 11.4 | 5.5 | 3.7 | 3.1 | 5.0 |
| C ₃ +C ₄ | 6.1 | 10.2 | 6.5 | 4.3 | 2.1 | 10.1 |
| C ₅ + | 86.9 | 78.4 | 88.0 | 92.0 | 94.8 | 84.9 |
| C ₅ +Vol. % Yield (100% Basis) | 86.5 | 78.0 | 86.7 | 92.2 | 95.1 | 83.7 |

TABLE VIII-5

REFORMING OF n-PARAFFIN-DOPED JP-7 JET FUEL

| <u>RUN</u> | <u>63-1</u> | <u>63-2</u> | <u>64-1</u> | <u>64-2</u> | <u>65-1</u> | <u>65-2</u> |
|--|-------------|-------------|-------------|-------------|-------------|-------------|
| <u>Catalyst - Gms.</u> | 35 | → | 17.5 | → | 17.5 | → |
| <u>Conditions</u> | | | | | | |
| Temp. °F | 850 | 910 | 880 | 880 | 850 | 910 |
| Pressure-PSIG | 500 | 500 | 500 | 500 | 500 | 500 |
| LHSV | 2 | 2 | 4 | 8 | 8 | 8 |
| H ₂ /H C | 5/1 | | | | | |
| <u>Liq. Prod. Analysis</u> | | | | | | |
| Freeze Pt (°F) | -90 | -90 | -79 | -78 | -45 | -90 |
| S | 76.1 | 56.6 | 65.4 | 68.0 | 73.0 | 60.1 |
| O | 1.5 | 1.6 | 1.4 | 1.9 | 2.3 | 2.4 |
| A | 22.4 | 41.8 | 33.2 | 30.1 | 24.7 | 37.5 |
| <u>SIM-D-Wt. %</u> | | | | | | |
| C ₅ -130 | 6 | 10 | 8 | 6 | 1 | 7 |
| 130-518 (JP4) | 91 | 87 | 88 | 89 | 91 | 87 |
| 330-572 (JP8) | 70 | 49 | 57 | 73 | 90 | 65 |
| 572+ | 0 | 0 | 1 | 1 | 0 | 1 |
| <u>Wt. Balance</u> | | | | | | |
| H ₂ +C ₁ +C ₂ | 4.60 | 6.79 | 6.20 | 3.81 | 2.83 | 4.20 |
| C ₃ +C ₄ | 7.58 | 16.80 | 7.90 | 5.69 | 4.27 | 9.58 |
| C ₅ + | 90.04 | 74.37 | 86.32 | 93.26 | 95.72 | 84.12 |
| Total | 102.22 | 97.96 | 100.42 | 102.76 | 102.82 | 97.90 |
| <u>Wt. Balance</u> | | | | | | |
| <u>Corrected to 100%</u> | | | | | | |
| H ₂ +C ₁ +C ₂ | 4.5 | 6.9 | 6.2 | 3.7 | 2.7 | 4.3 |
| C ₃ +C ₄ | 7.4 | 17.1 | 7.8 | 5.5 | 4.1 | 9.8 |
| C ₅ + | 88.1 | 76.0 | 86.0 | 90.8 | 93.2 | 85.9 |
| C ₅ +Vol. % Yield (100% Basis) | 91.5 | 75.1 | 87.0 | 93.2 | 95.5 | 88.0 |

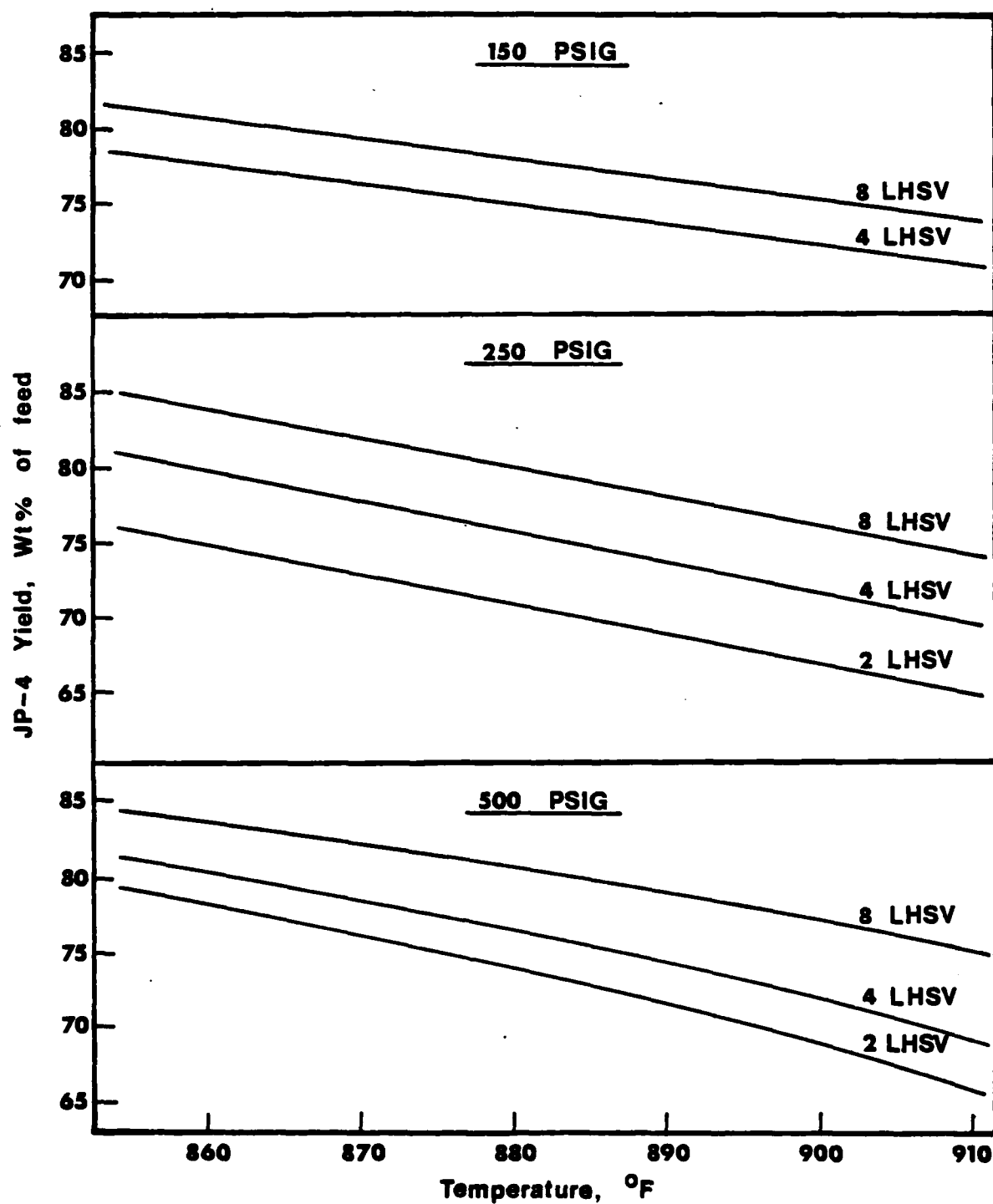


Figure VIII-1. Effect Of Temperature On JP-4
Yield During Reforming Of n-Paraffin-Doped JP-7
Jet Fuel

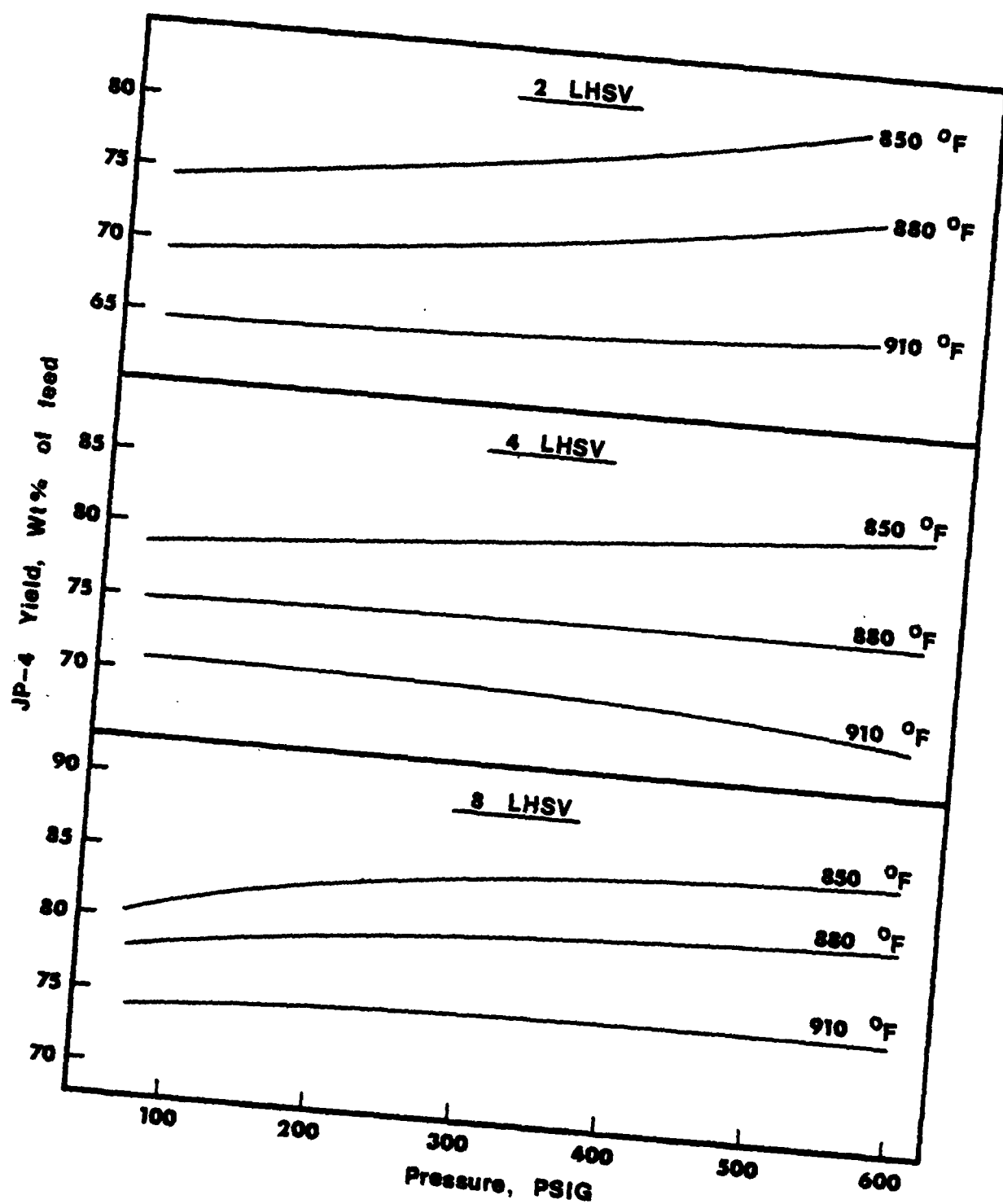


Figure VIII-2. Effect Of Pressure On JP-4 Yield
During Reforming Of n-Paraffin-Doped JP-7
Jet Fuel

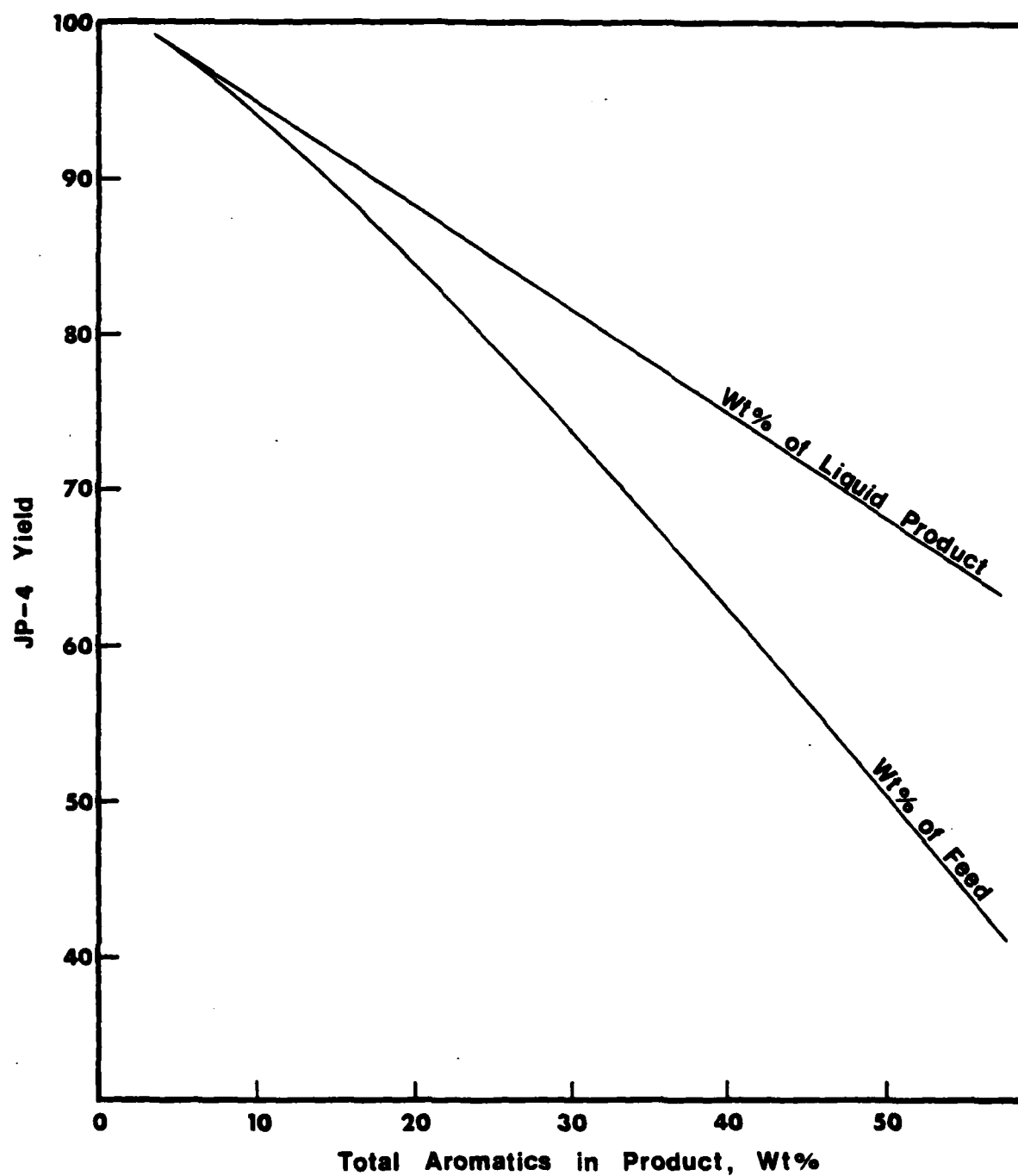


Figure VIII-3. Dependence Of JP-4 Yield - As Both
Wt. % Of Liquid Product And As Wt. % Of Feed - On
Product Aromatic Content During Reforming Of
Paraffin-Doped JP-7 Fuel

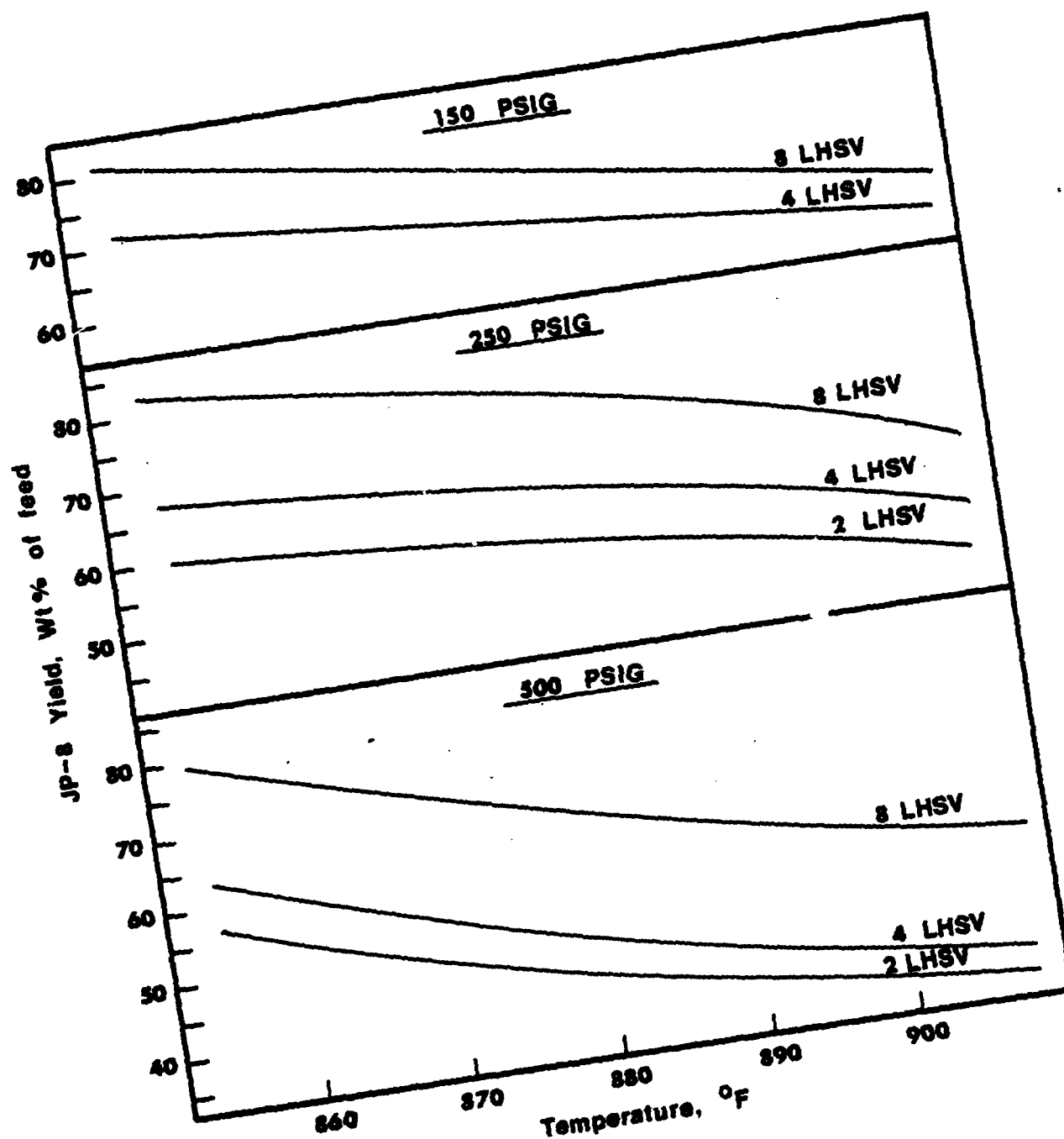


Figure VIII-4. Variation Of JP-8 Yield With Temperature During Reforming Of n-Paraffin-Doped JP-7 Jet Fuel.

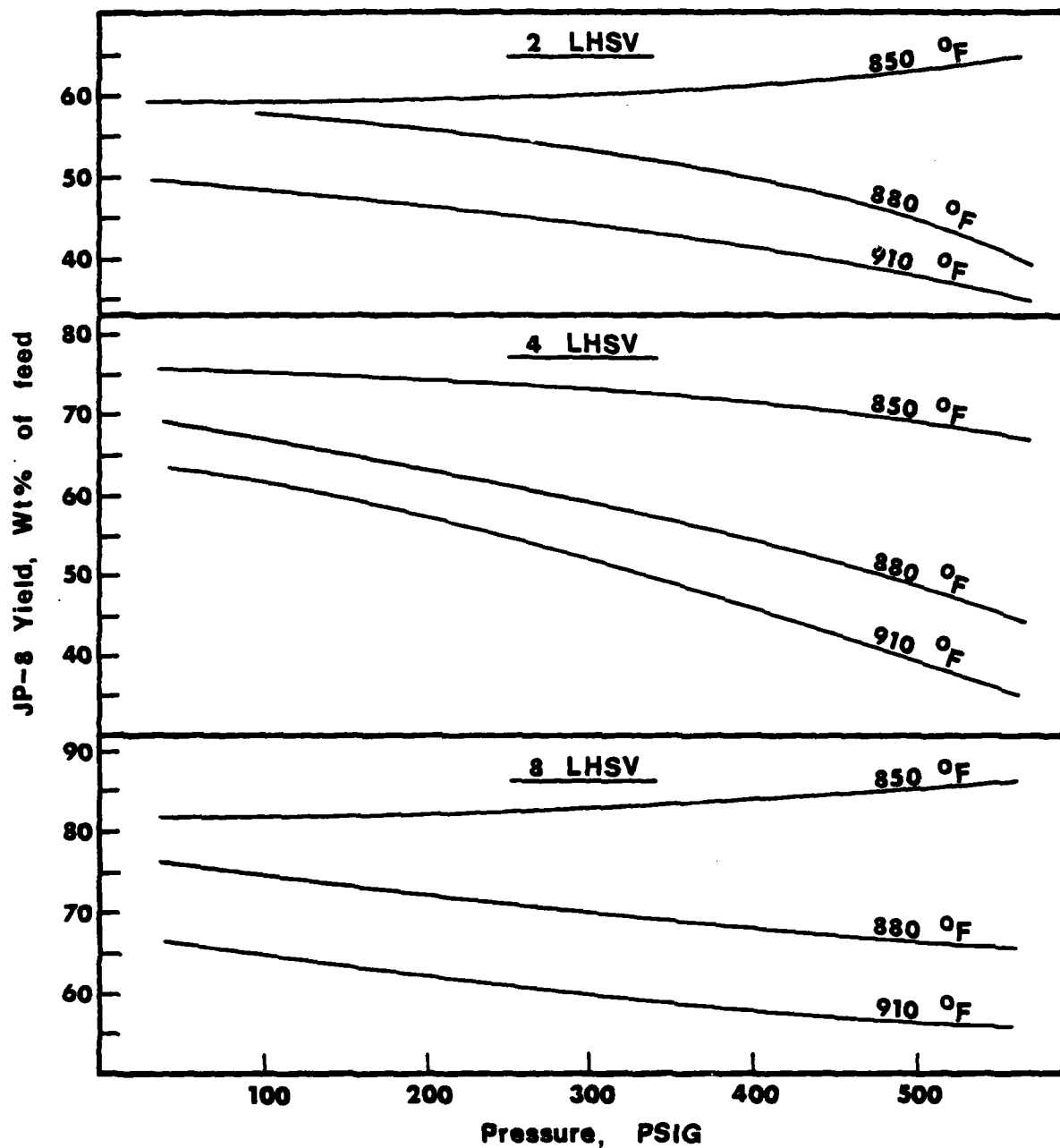


Figure VIII-5. Variation Of JP-8 Yield With Pressure During Reforming Of n-Paraffin-Doped JP-7 Jet Fuel

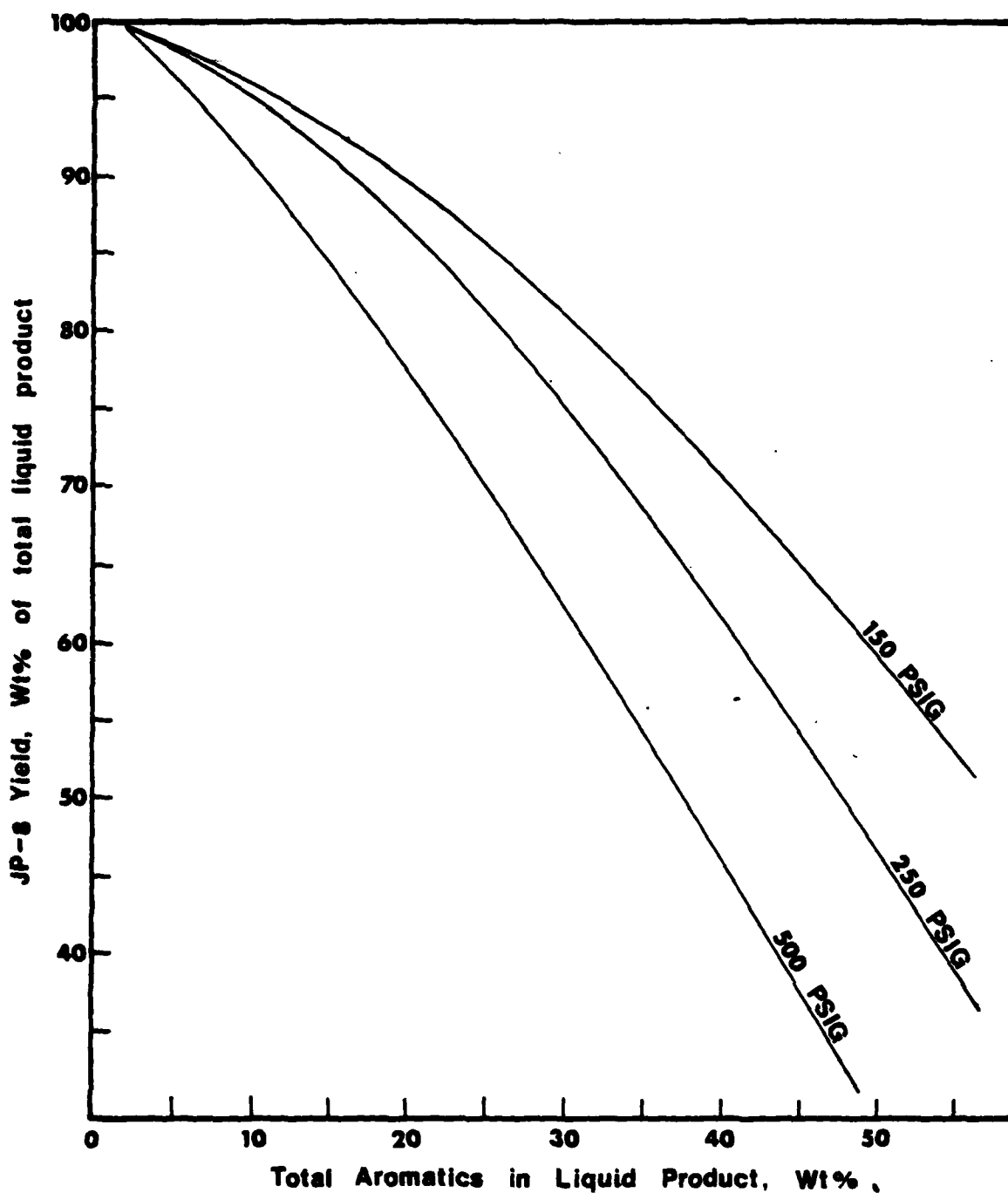


Figure VIII-6. Dependence Of JP-8 Yield - As Wt. % Of Liquid Product - On Product Aromatic Content During Reforming Of n-Paraffin-Doped JP-7 Jet Fuel

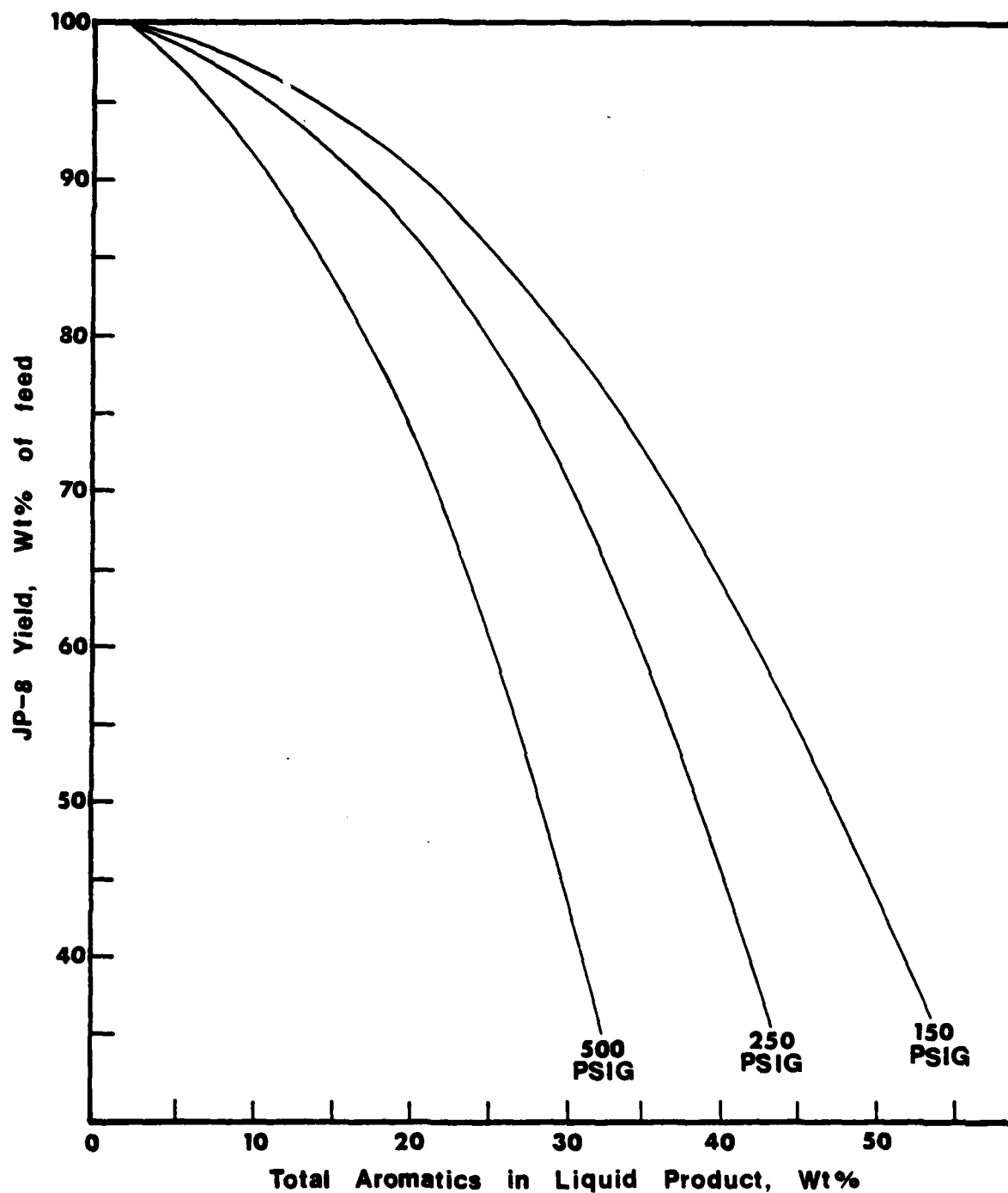


Figure VIII-7. Dependence Of JP-8 - As Wt. % Of Feed - On Product Aromatic Content During Reforming Of n-Paraffin-Doped JP-7 Jet Fuel

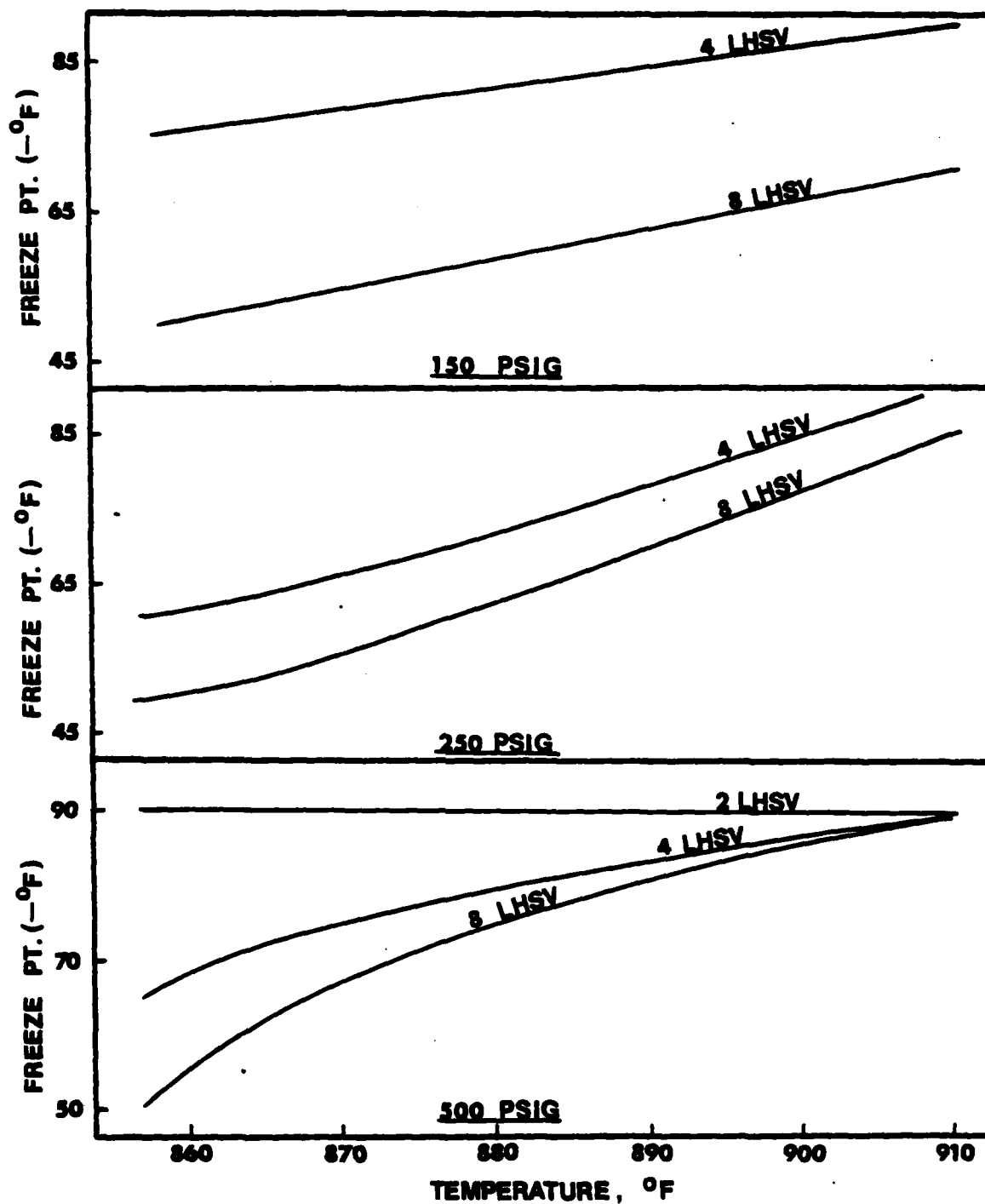


Figure VIII-8. Effect Of Temperature On Product Freeze Point During Reforming Of n-Paraffin-Doped JP-7 Jet Fuel

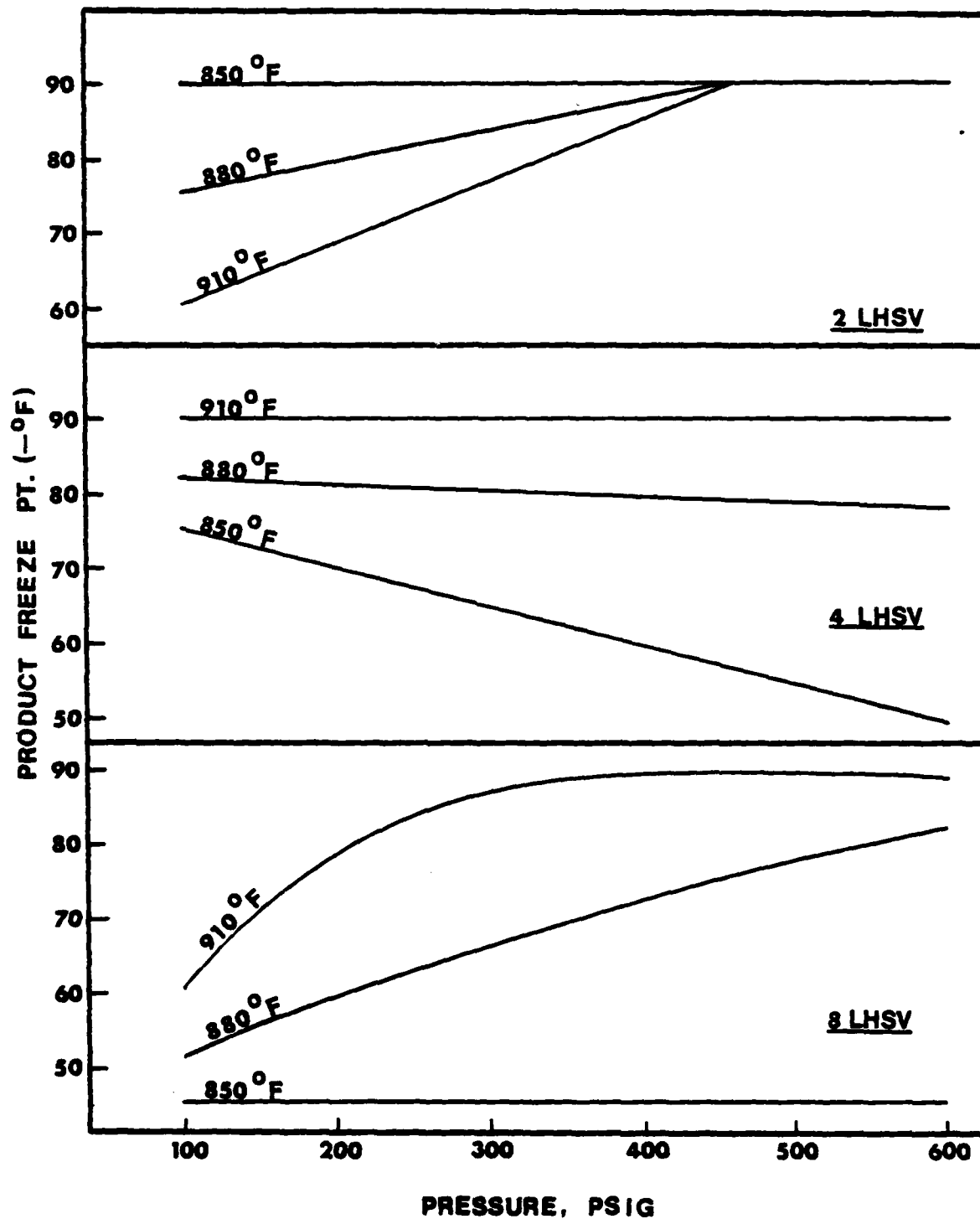


Figure VIII-9. Effect Of Pressure On Product Freeze Point During Reforming Of n-Paraffin-Doped JP-7 Jet Fuel

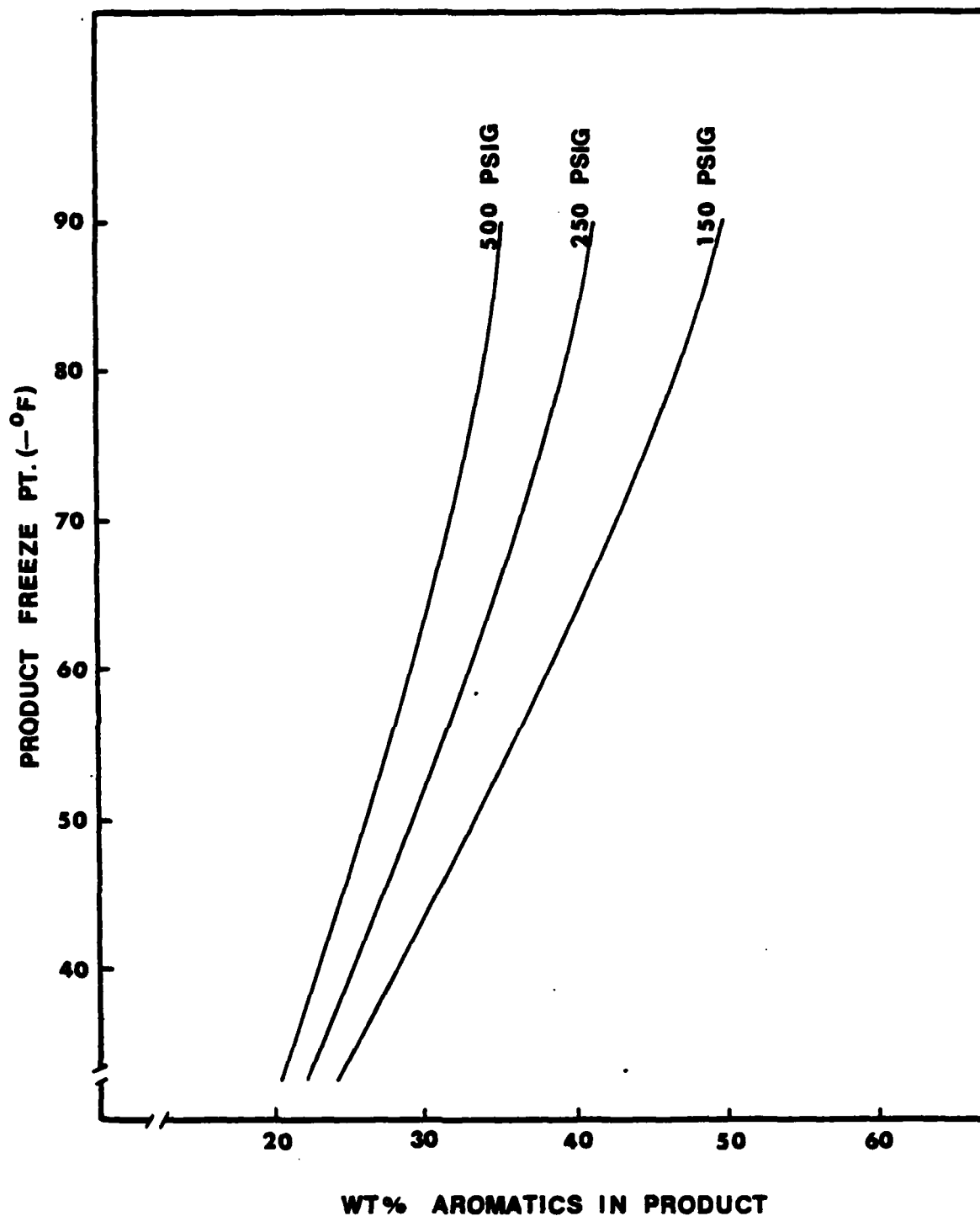


Figure VIII-10. Dependence Of Product Freeze Point On Product Aromatic Content During Reforming Of n-Paraffin-Doped JP-7 Jet Fuel

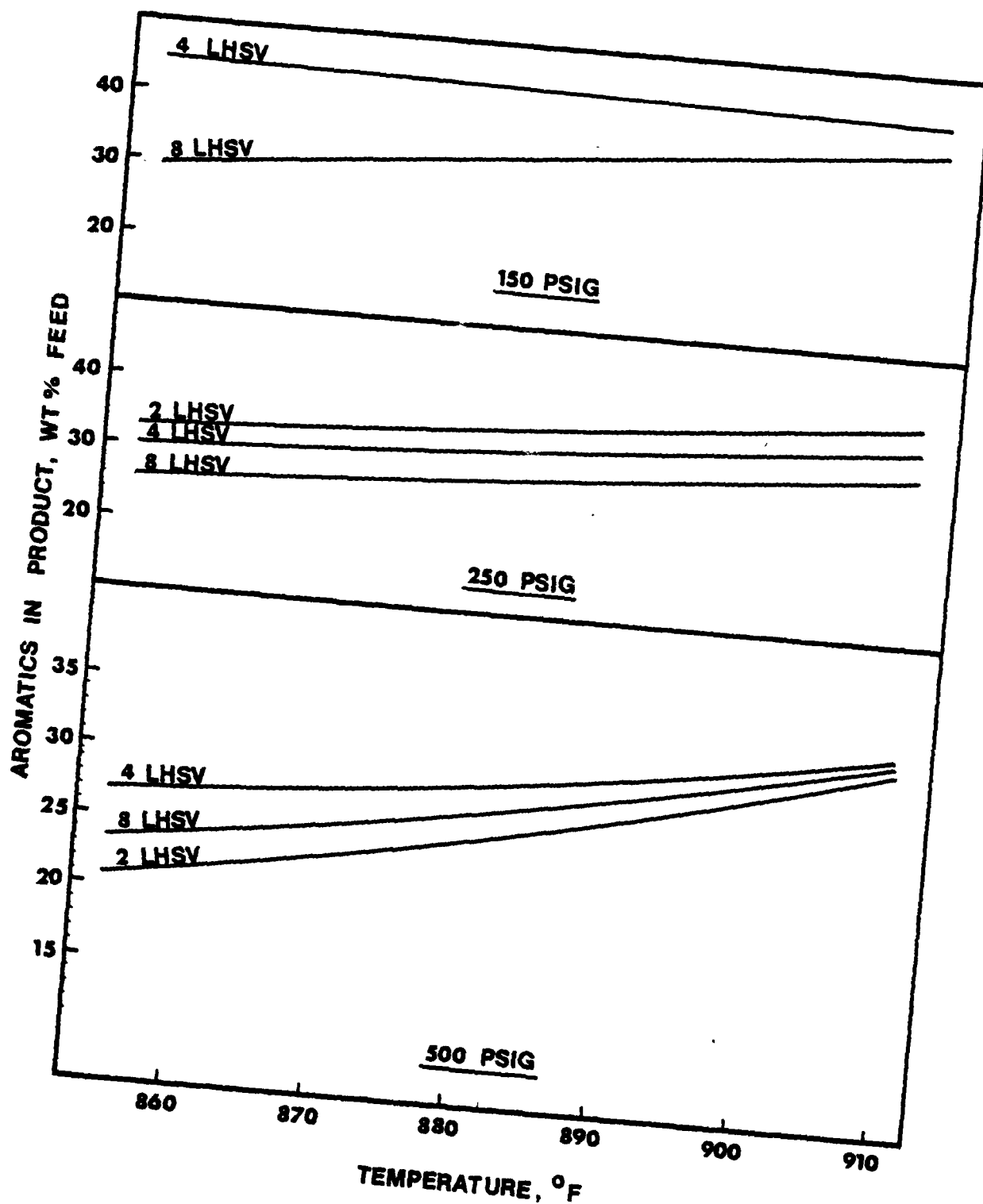


Figure VIII-11. Effect Of Temperature On Product Aromatic Content - As Wt. % Of Feed - During Reforming Of n-Paraffin-Doped JP-7 Jet Fuel

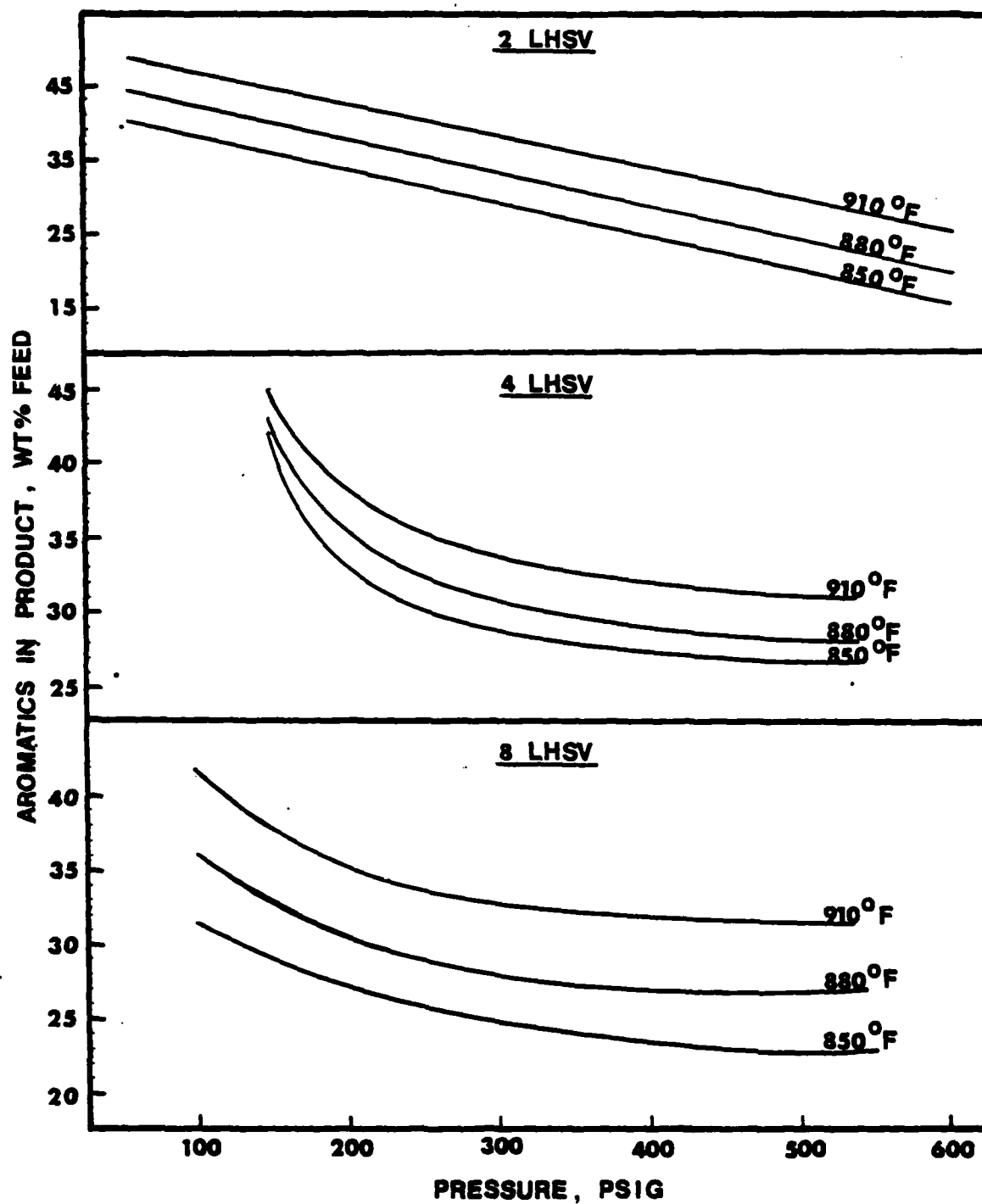


Figure VIII-12. Effect Of Pressure On Product Aromatic Content - As Wt. % Of Feed - During Reforming Of n-Paraffin-Doped JP-7 Jet Fuel

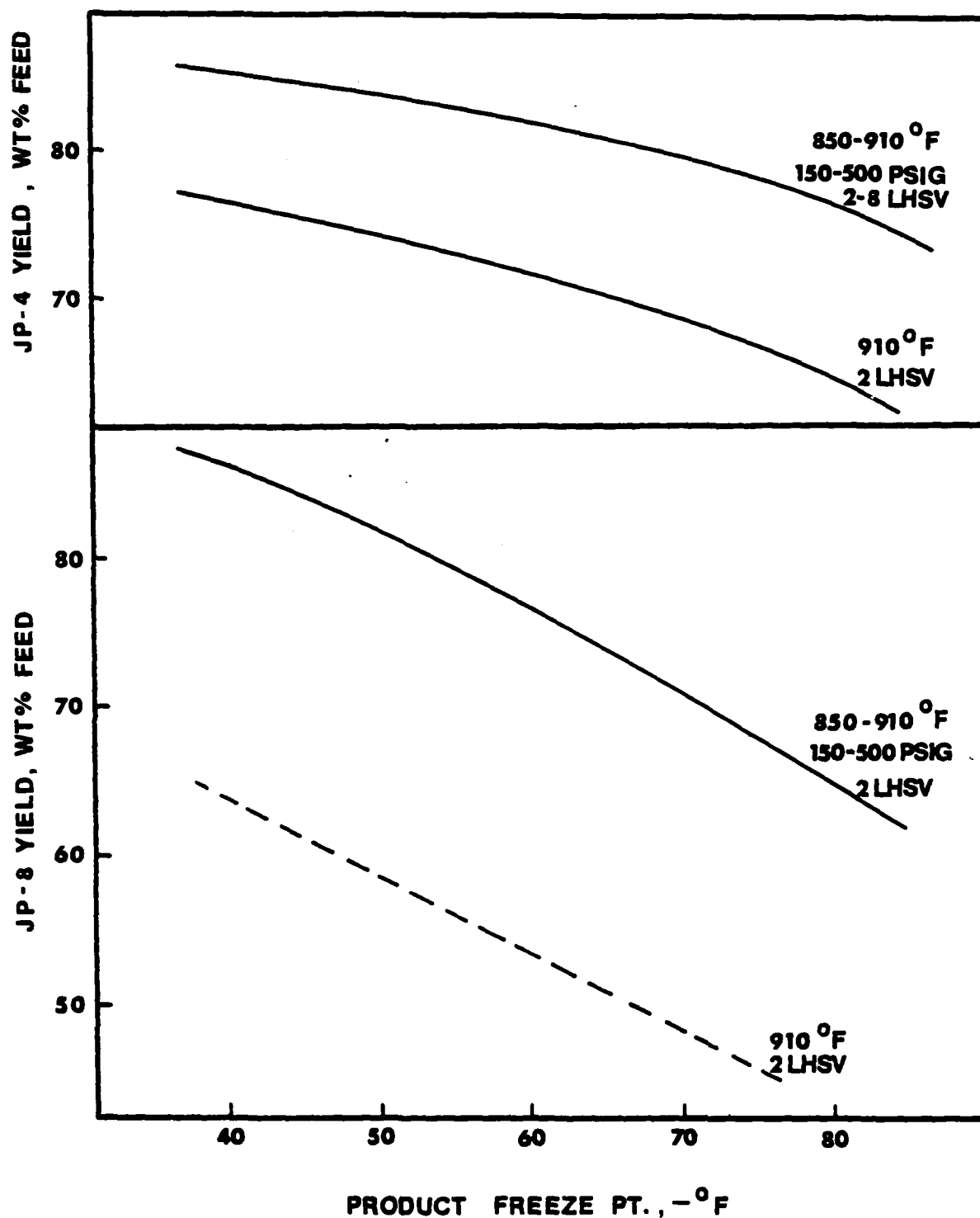


Figure VIII-13. Variation Of JP-4 And JP-8 Yield -
As Wt. % Of Feed - With Product Freeze Point
During Reforming Of n-Paraffin-Doped JP-7 Jet Fuel.

The reforming of a n-paraffin containing jet fuel at two sets of process conditions was also accomplished. The results are given in the attached Tables VIII-6 and VIII-7. Table VIII-6 lists the results obtained by reforming at 850°F, 500 psig, and 8 LHSV over a Pt/Re catalyst. The properties (freeze point, aromatic content) of the reformate were measured and the total reformate then fractionated to yield a JP-4 jet fuel (130-518°F) and a JP-8 fuel (330-527°F). The properties of each fraction were measured. The jet fuel fraction was then subjected to mild hydrogenation and the properties remeasured.

A second reforming test (Table VIII-7) was performed at 880°F, 250 psig, and 8 LHSV over the same catalyst and the same sequence of property measurement and hydrogenation was followed as outlined above. The best results considering yield of total product, aromatic content, and lowered freeze point for both JP-4 and JP-8 fractions were obtained at the second set of conditions listed in Table VIII-7. The JP-4 fraction contained 34 weight percent aromatics and had a freeze point of -78°F which, upon mild hydrogenation, yielded a JP-4 fraction containing 21 weight percent aromatics with a freeze point of -70°F. The JP-8 fraction contained 45 weight percent aromatics and had a freeze point of -67°F which, upon mild hydrogenation, yielded a fraction containing 29 weight percent aromatics with a freeze point of -65°F.

TABLE VIII-6
REFORMING OF JET FUEL
CONTAINING n-PARAFFIN

| <u>Run 416</u> | <u>68</u> | <u>68A</u> | <u>74</u> | <u>68B</u> | <u>75</u> |
|--|-----------|--|----------------------|--|----------------------|
| <u>Operation</u> | Reforming | Distillation of Product from Run 68 to Yield JP-4 | Hydrog. of 68A | Distillation of Product from Run 68 to Yield JP-8 | Hydrog. of 68B |
| <u>CONDITIONS</u> | | | | | |
| Temp. °F | 850 | 130-518°F | 500 | 330-572°F | 500 |
| Pressure PSIG | 500 | | 200 | | 200 |
| LHSV | 8 | | 2 | | 2 |
| H ₂ /H'C | 5/1 | | 10/1 | | 10/1 |
| <u>PRODUCT</u> | | | | | |
| Freeze Point °F | -58 | -61.6 | -59.8 | -50.8 | -54.4 |
| <u>FIA</u> | | | | | |
| S | 74.9 | 72.0 | 98.3 | 69.5 | 86.9 |
| O | 1.1 | 1.9 | 0.7 | 1.4 | 0.8 |
| A | 24.0 | 26.1 | 1.0 | 29.1 | 12.3 |
| <u>CORRECTED TO 100%</u> | | | | | |
| <u>WT. BALANCE-WTZ FEED</u> | | | | | |
| H ₂ - C ₁ - C ₂ | 4.4 | | | | |
| C ₃ - C ₄ | 6.2 | | | | |
| C ₅ + | 89.4 | | | | |
| <u>C₅ + VOL% YIELD</u> | | | | | |
| | 90.3 | | 106 | | 106 |
| <u>CORRECTED TO 100%</u> | | | | | |

TABLE VIII-7
REFORMING OF JET FUEL
CONTAINING n-PARAFFIN

| <u>Run 416</u> | <u>69</u> | <u>69A</u> | <u>76</u> | <u>69B</u> | <u>77</u> |
|--|-----------|--|----------------------|--|----------------------|
| <u>Operation</u> | Reforming | Distillation of Product from Run 69 to Yield JP-4 | Hydrog. of 69A | Distillation of Product from Run 69 to Yield JP-8 | Hydrog. of 69B |
| <u>CONDITIONS</u> | | | | | |
| Temp. °F | 880 | | 500 | | 500 |
| Pressure PSIG | 250 | 130-518°F | 200 | 330-572°F | 200 |
| LHSV | 8 | | 2 | | 2 |
| H ₂ /H'C | 5/1 | | 10/1 | | 10/1 |
| <u>PRODUCT</u> | | | | | |
| Freeze Point °F | -74.2 | -77.8 | -70.6 | -67 | -65.2 |
| <u>FIA</u> | | | | | |
| S | 66.4 | 63.3 | 77.2 | 50.9 | 70.2 |
| O | 2.2 | 2.4 | 1.3 | 4.3 | 0.8 |
| A | 31.4 | 34.3 | 21.5 | 44.8 | 29.0 |
| <u>CORRECTED TO 100%</u> | | | | | |
| <u>WT. BALANCE-WTZ FEED</u> | | | | | |
| H ₂ - C ₁ - C ₂ | 3.6 | | | | |
| C ₃ - C ₄ | 5.2 | | | | |
| C ₅ ⁺ | 91.2 | | | | |
| <u>C₅ + VOL% YIELD</u> | | | | | |
| | 93 | | 103 | | 103 |
| <u>CORRECTED TO 100%</u> | | | | | |

DISCUSSION

The reforming carried out in this study was atypical reforming or high-endpoint reforming since the IBP of the feedstock used in this study is the endpoint for typical naphthas processed in petroleum catalytic reformers. Many of the correlations follow the typical graphs that are representative for petroleum reforming. However, there are a few isolated areas that appear abnormal. These can be explained on the basis of: (1) the data developed for these points may be erroneous, however, it should be remembered that the data correlated in other areas, or (2) atypical reforming reactions were occurring due to the high boiling character of the feed; these reactions would include partial dehydrogenation of the bicyclic naphthenes, dehydrogenation of one ring of a bicyclic followed by hydrocracking of the other naphthenic ring or vice versa to yield an alkylbenzene, dehydrocyclization of n-paraffins to yield a bicyclic aromatic or naphthene, dehydroisomerization of a naphthene to an indan, hydrocracking of a hydrindane to yield an alkylcyclopentane, selective cracking-isomerization of the n-paraffins, etc. All of these, plus other reactions, could lead to the abnormalities seen in some of the graphical interpretation of these data.

The main purpose of this work, as mentioned earlier, was to define a set or sets of conditions for reforming a n-paraffin containing petroleum based jet fuel to yield

sufficient quantities of product for more detailed analysis. This large sample of reformat would be fractionated to yield JP-4 and JP-8 jet fuel fractions. These two fractions would contain a high percentage of aromatics (20-30 weight percent versus less than 5 percent in JP-7) and, hopefully, have a freeze point below -45°F. If these fractions of jet fuel do not meet freeze point specifications while containing a high concentration of aromatics, then hydrogenation of the aromatics to naphthenes would be utilized to attain this end. It should be remembered that in the case of the reforming step an attempt is made to maximize the selective cracking and isomerization properties of the catalyst for the conversion of n-paraffins in addition to its cyclization properties.

The parameters that will determine the best process conditions from this study and correlation are as follows: maximize JP-8 yield, achieve a freeze point below -45°F, and maintain an aromatic content in the product of 20-30 weight percent. Maximum JP-8 yield was determined as follows:

| <u>FIGURE</u> | <u>TEMPERATURE</u> <u>°F</u> | <u>PRESSURE</u> <u>PSIG</u> | <u>LHSV</u> | <u>JP-8 YIELD</u> |
|---------------|---------------------------------|--------------------------------|-------------|-------------------|
| IX-4 | 850 | 150 | 8 | 82 |
| IX-4 | 850 | 250 | 8 | 83 |
| IX-4 | 850 | 500 | 8 | 84 |
| IX-5 | Substantiates above values | | | |

JP-8 yield versus weight percent aromatics in product (Figure VIII-12) indicates the following range of conditions to yield 20-30 weight percent aromatics: 150-250 psig at 8 LHSV. The process conditions required to yield a freeze point of -45°F or lower are found in Figure VIII-8. A broad range of conditions exist that yield a freeze point of -45°F or lower, thus this parameter will be correlated with the aromatics and JP-8 yield. An examination of the data indicated five sets of conditions exist that deserve consideration in the EXTRACTACRACKING scheme and two sets were selected for further study as indicated below.

| PROCESS CONDITIONS | | | JP-8 YIELD WT. % FEED | F.P. °F | PERCENT AROMATICS IN PRODUCT |
|--------------------|----------|------|-----------------------------|------------|------------------------------------|
| TEMPERATURE °F | PRESSURE | LHSV | | | |
| 850 | 500 | 8 | 84 | -45 | 21 |
| 880 | 500 | 8 | 66 | -75 | 29 |
| 850 | 250 | 8 | 83 | -45 | 24 |
| 880 | 250 | 8 | 75 | -62 | 30 |
| 850 | 150 | 8 | 82 | -46 | 30 |

The two sets of conditions selected for further study are as follows:

850°F - 500 psig - 8 LHSV

In the PV study this set yielded a JP-8 fraction of 84 weight percent containing 20 weight percent aromatics with a freeze point of -45°F

880°F - 250 psig - 8 LHSV

This set was chosen because aromatic content of product is increased to 30 weight percent and the freeze point is lowered to -62°F.

2. M-SERIES

SUMMARY

Studies were performed, at single conditions determined from the simulation studies described in Part 1 of this section, on freeze point modification of one JP-4 and one JP-8 sample derived from in situ shale oils. Freeze point reductions of 23 and 12°F were obtained at comparable operating conditions, signifying that the heavier JP-8 fraction may require higher severity operations for comparable freeze point reduction effectiveness.

OBJECTIVES

Objectives for these studies were to: (1) modify the freeze point of potential Air Force fuel samples, (2) determine the comparison between simulated and actual sample processing response and (3) derive a complete freeze point modification yield structure for each sample.

EQUIPMENT AND EXPERIMENTAL

Procedures and equipment utilized for these studies were identical to those described in Part 1 of this section.

FEEDSTOCK

Feedstocks for these studies were rehydrotreated samples M-112 and M-121 from the previously described guard-case studies. Guardcase product from M-112 was fractionated to a nominal 510°F atmospheric still overhead temperature in preparation for reforming. The M-121 sample was stabilized and reformed as a broad-range (C₆-600°F) feed. Properties of both the as-charged feedstock and pertinent fractions are shown in Table VIII-8.

RESULTS

Pertinent conditions and material balance data are shown in Table VIII-9. Excellent closures, liquid recovery and operating stability were attained.

DISCUSSION

These runs demonstrated the feasibility of modifying turbine fuel freeze point by these methods. Surprisingly, these materials demonstrated essentially equivalent C₅+ liquid yields. As might be expected, there was a slight hydrogen yield advantage (0.3 weight percent of feed) to the lighter M-112 sample.

Of particular interest to this study, properties of the pertinent fractions for both feed and product are shown

TABLE VIII-8

MILITARY JET FUEL FROM SHALE OIL
SAMPLE PREPARATION SEQUENCE

| | M-112 | | | M-121 | | | GC-1 | | |
|----------------------------|----------|-------|----------|----------|-------|----------|------|------|----------|
| | GC | REF. | AR. SAT. | GC | REF. | AR. SAT. | GC | REF. | AR. SAT. |
| AROMATICS, WT% | 26.0 | 45.8 | 18.3 | 30 | 39.9 | 20.4 | 23 | 42.3 | 11.9 |
| GRAVITY, °API | 43.7 | 39.8 | 46.7 | 39.1 | 37.0 | 46.6 | 42.4 | 39.6 | 44.2 |
| HYDROGEN, WT% | 18 smoke | 12.7 | 14.6 | 17 smoke | 12.3 | 13.9 | - | 12.7 | 14.2 |
| FREEZE POINT, °F | -56 | -78.7 | -81.4 | -33.7 | -46.3 | -46.3 | -31 | -49 | -48.1 |
| D-86 DIST., °F @ 10% INP | 186 | --- | 218 | --- | 350 | 346 | --- | --- | 240 |
| 10 VOL % | 272 | --- | 266 | --- | 380 | 384 | --- | --- | 300 |
| 20 | 322 | --- | 314 | --- | 396 | 400 | --- | --- | 330 |
| 50 | 404 | --- | 379 | --- | 456 | 445 | --- | --- | 403 |
| 90 | 464 | --- | 454 | --- | 550 | 523 | --- | --- | 492 |
| KP | 484 | --- | 490 | --- | 586 | 560 | --- | --- | 522 |
| D-2887 DIST., °F @ 10% INP | --- | 79 | 151 | --- | 109 | 254 | 160 | 95 | 112 |
| 10 WT % | --- | 244 | 244 | --- | 241 | 340 | 285 | 269 | 238 |
| 20 | --- | 295 | 290 | --- | 302 | 375 | 333 | 321 | 287 |
| 50 | --- | 403 | 391 | --- | 430 | 447 | 433 | 418 | 387 |
| 90 | --- | 507 | 482 | --- | 561 | 556 | 543 | 541 | 504 |
| KP | --- | 631 | 619 | --- | 717 | 661 | 587 | 674 | 631 |
| VAPOR PRESSURE, PSI | 0.85 | --- | --- | --- | --- | --- | --- | --- | --- |
| FLASH POINT, °F | --- | --- | --- | 145 | --- | --- | --- | --- | --- |
| NITROGEN, PPM | --- | --- | --- | --- | --- | --- | <1 | --- | --- |
| SULFUR, PPM | --- | --- | --- | --- | --- | --- | <1 | --- | --- |
| SATURATES, VOL % | --- | --- | --- | --- | --- | --- | 77.0 | --- | --- |
| OLEFINS, VOL % | --- | --- | --- | --- | --- | --- | 0.3 | --- | --- |

TABLE VIII-9

M-SERIES FREEZE POINT MODIFICATION

| Sample | M 112 | | M 121 |
|--------------------------------|--------|--|--------|
| OPERATING CONDITIONS | | | |
| Temperature, °F | 850 | | 850 |
| Pressure, PSIG | 500 | | 500 |
| LHSV, Hr ⁻¹ | 8.0 | | 8.0 |
| H ₂ /HC Molar Ratio | 5.0 | | 5.0 |
| MATERIAL BALANCE | | | |
| Weight Percent of Feed | | | |
| H ₂ , NET | 1.42 | | 1.15 |
| C ₁ | 0.38 | | 0.38 |
| C ₂ | 0.54 | | 0.57 |
| C ₃ | 1.03 | | 1.09 |
| C ₄ | 0.87 | | 0.90 |
| C ₅ | 0.39 | | 0.54 |
| Stabilized Liquid | 95.52 | | 95.40 |
| | | | |
| Closure | 100.15 | | 100.03 |

in Table VIII-8. These properties represent the entire product fraction for M-112 and the nominal 310°F+ fraction of M-121. The JP-4 target (M-112) sample demonstrates a tremendous 23°F freeze point depression with a +20 percent aromatics gain. The resulting freeze point of -79°F is even more impressive in view of the low volatility (0.8 RVP) of the feed sample. The JP-8 target (M-121) demonstrated a lesser freeze point depression (12°F), indicating that these higher boiling materials may require higher severity operations than the JP-4 products. The aromatics gain of +10 percent was also less than the JP-4 sample.

While these data are not of sufficient breadth and quantity to allow correlation, there is an apparent good agreement between these two samples for aromatics and freeze point. As noted above, a 20 percent aromatics gain provided a -23°F freeze point change; the 10 percent aromatics gain provided a -12°F change. On this basis, for these samples, the apparent correlation would then be a freeze point depression of 1.2°F for each 1 percent gain in aromatic content through the reformer. This compares to a 2.4°F lowering of freeze point for each 1 percent gain in aromatics during the simulation studies (without fractionation).

RECOMMENDATIONS AND CONCLUSIONS

- Freeze point modification was demonstrated for both JP-4 and JP-8 turbine fuels.

- Complete module yield structures were defined, with both samples demonstrating >95 weight percent yield.
- Freeze point reduction for actual shale samples, on a °F per percent aromatics change basis, is roughly half of that demonstrated for simulated (non-fractionated) materials.
- Extremely low freeze point for the JP-4 sample was obtained, particularly impressive since the sample also demonstrated low volatility.

3. ACCELERATED AGING

SUMMARY

GC-1 guardcase product was reformed under accelerated aging conditions to examine preliminary aging parameters for a selected catalyst system. Results, which would nominally correspond to roughly two months of operation for petroleum naphtha, demonstrated satisfactory stability, although aging was encountered during the last half of the run.

OBJECTIVES

Objectives for this study were: (1) to examine, on a preliminary basis, initial catalyst deactivation rates and (2) to produce material for further processing.

EQUIPMENT AND PROCEDURE

Equipment utilized for this study was identical to that used for Parts 1 and 2 of this study. Experimental

procedure was changed so that a smaller catalyst charge could be used at higher throughputs and effective severity to accelerate the aging process. Conditions selected were:

910°F

500 psig

24 LHSV

5:1 Hydrogen:Hydrocarbon Ratio

Under petroleum naphtha reforming conditions, the severity differential provided by these parameters would correspond to approximately two months of commercial operation after 32 hours on stream for this experiment. This correlation is not, of necessity, valid for the shale feedstock used, but does serve to indicate the magnitude of acceleration involved.

FEEDSTOCK

Feedstock for this run was guardcase product from Run GC-1. The full-range guardcase product was fractionated to a nominal 580°F overhead to remove excessive heavy ends which could cause erroneously high deactivation rates in this study. Properties of the feedstock are shown in Table VIII-8.

RESULTS

Results for this study are shown in Table VIII-10, as obtained by experimental measurement.

TABLE VIII-10

GC-1 ACCELERATED AGING

| Period | 1 | 2 | 3 | 4 | 5 | Total |
|------------------------------|-------|-------|-------|-------|-------|-------|
| OPERATING CONDITIONS | | | | | | |
| Temperature, °F | 910 | | | | | |
| Pressure, PSIG | 500 | | | | | |
| LHSV, Hr ⁻¹ | 24 | | | | | |
| H ₂ /HC Ratio | 5.0 | | | | | |
| MATERIAL BALANCE | | | | | | |
| Weight Percent of Feed | | | | | | |
| H ₂ | 1.52 | 1.49 | 1.36 | 1.02 | 0.99 | 1.29 |
| C ₁ | 0.78 | 0.93 | 1.36 | 1.69 | 1.07 | 1.17 |
| C ₂ | 1.84 | 1.48 | 2.81 | 2.88 | 0.79 | 2.00 |
| C ₃ | 2.89 | 2.36 | 0.03 | 0.75 | 1.32 | 1.48 |
| C ₄ | 1.99 | 1.65 | 3.24 | 0.41 | 1.03 | 1.74 |
| C ₅ | 1.13 | 1.65 | 2.66 | 0.67 | 0.96 | 1.58 |
| Stabilized Liquid | 94.08 | 96.13 | 94.23 | 94.28 | 91.49 | 94.13 |
| Closure | 104.2 | 105.1 | 104.5 | 101.5 | 97.3 | 102.7 |
| Hours on Stream | 6 | 12 | 18 | 24 | 29 | - |
| Hydrogen Production, SCFB | | | | | | |
| PRODUCT PROPERTIES | | | | | | |
| Saturates | 54.5 | 51.1 | 54.4 | 58.3 | 56.3 | - |
| Olefins | 0.6 | 0.9 | 0.7 | 0.5 | 0.8 | - |
| Aromatics | 44.9 | 48.0 | 44.9 | 41.2 | 42.9 | - |

DISCUSSION

Some deactivation was observed during the run. Figure VIII-14 presents (normalized) data for hydrogen production, C₅+ liquid yield and liquid product aromatic content. As the aging occurred, hydrogen yields decreased, liquid product yield increased and aromatics content decreased as expected. There may have been some experimental problem during the period ending in hour 24, as hydrogen yield and aromatics content improved during the next period. Unfortunately, the supply of feed was exhausted in hour 29 and no further data could be obtained.

The deactivation rates demonstrated appear to be quite acceptable though higher than encountered in conventional petroleum reforming. Assuming the freeze point/aromatics correlation developed during Part 2 of this section pertains, the loss in freeze point depression (hour 6 to hour 29) is only 1°F.

RECOMMENDATIONS AND CONCLUSIONS

- Aging behavior of the freeze point modification module was shown to be moderate and gradual.
- Sample was produced for further processing.

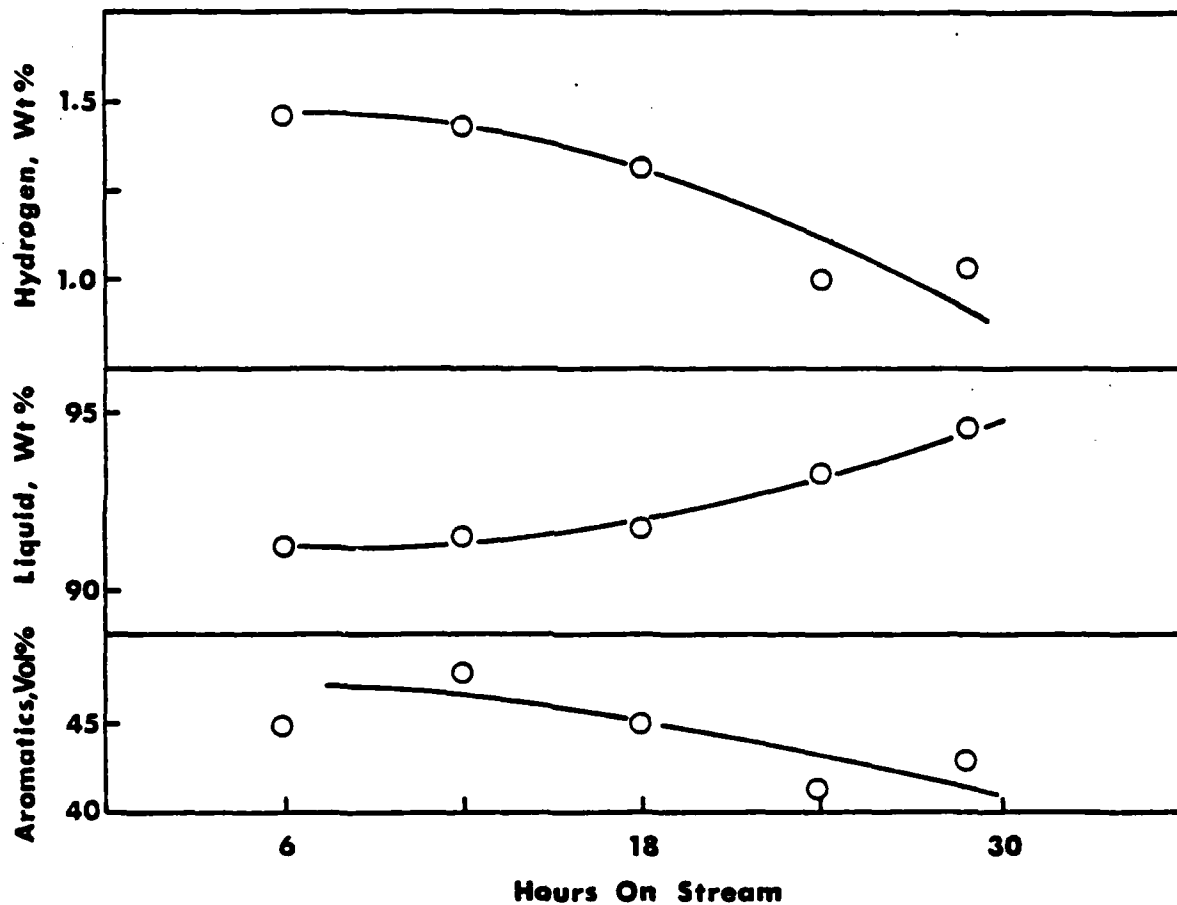


Figure VIII-14. Accelerated Aging Response Of Sample GC-1 (Normalized Data)

SECTION IX

AROMATIC SATURATION

SUMMARY

Three potential turbine fuel samples were processed through an aromatic saturation unit to produce aromatic specification materials. For feed aromatic contents of 45.8, 39.9 and 42.3 volume percent, aromatic saturation products of 18.3, 20.4 and 11.9 volume percent were obtained. Freeze point changes were minor, ranging from +1 to -3°F. Some loss of catalyst activity was noted in the longer runs.

OBJECTIVES

These studies were designed to: (1) determine the effectiveness of Ashland's aromatic saturation process, (2) determine freeze point, product property and product yield response to process parameters and (3) determine the interactions between freeze point modification and aromatic saturation for JP-4 and JP-8 fractions.

EQUIPMENT

These experiments were performed in a 316 stainless steel 1" I.D. Universal reactor heated by a radiant heat furnace. The temperatures were controlled through the use of Thermo Electric Selectrol switches and measured by means of a Honeywell temperature indicator and Iron-Constantan thermocouples located throughout the reactor (preheat, catalyst bed, postheat).

The feed was metered from a capped (air bleed equalizer) graduate via a Lapp pump. The hydrogen was metered to the reactor through a Brooks continuous flow electronic equalizer. The effluent gas was separated from the liquid product in a Jerguson liquid level gauge and depressured to atmospheric pressure through a Grove pressure regulator. The effluent gas and any light gases from the liquid (after discharging to atmospheric pressure in a closed system) were passed through two acetone-dry ice traps and then measured by means of a wet test meter. The material collected in the dry ice traps and the liquid product were combined and stabilized to a 5°C overhead to yield a C₅+ reformat. Spot gas samples were taken during various periods of the test cycle, submitted for gas chromatographic analysis and the values averaged and normalized to yield a light gas value for each experiment.

FEEDSTOCKS

Feedstock for these runs were reformer products from runs M-112, M-121 and GC-1. All except M-121 were whole reformer product, while M-121 was a nominal 310°F+ reformat. Properties of these materials are shown in Table VIII-8.

PROCEDURE

The Universal 1" I.D. reactor was packed with 35 grams (50-ml) of Pt/Al catalyst in a normal downflow pseudologarithmic manner. Tabular alumina was used for preheat and postheat sections.

Hydrogen was allowed to flow over the catalyst overnight while the temperature was maintained at 750°F. After reduction of the catalyst, feed was introduced and the reaction zone was controlled at 500°F. Hydrogen flow was maintained at 5.2 SCFH. After a two hour lineout period, product was collected and data taken for eight hour material balance periods until all feed material was used. Refractive index was monitored to confirm activity. The conditions of the runs were as follows:

| | |
|------------------|-----------------|
| Temperature: | 500°F |
| Pressure: | 200 psig |
| LHSV: | 2.0 (100cc/hr) |
| H ₂ : | 10/1 (5.2 SCFH) |

RESULTS

The M-Series samples were saturated at the conditions outlined in the procedure. An average material balance closure for the five periods was 99.69 weight percent overall and a liquid yield of 103.6 volume percent was obtained. Hydrogen consumption was 906.5 SCFB for Run M-112 and 837 SCFB for Run M-121. Freeze point was lowered from -78.7 to -81.4°F for M-112 with no change occurring for M-121. The GC-1 run consumed an average of 780 SCFB H₂ and its freeze point was lowered from -48 to -48.1°F. Analytical results are given in Table IX-1.

TABLE IX-1

ANALYTICAL RESULTS FOR AROMATIC SATURATED PRODUCTS

| SAMPLE | M-112 | M-121 | GC-1 |
|---------------------------|-------|-------|-------|
| ANALYTICAL RESULTS | | | |
| API GRAVITY | 46.7 | 46.6 | 44.2 |
| SATURATES, Vol% | 80.3 | 78.6 | 87.9 |
| OLEFINS, Vol% | 1.4 | 1.0 | 0.2 |
| AROMATICS, Vol% | 18.3 | 20.4 | 11.9 |
| HYDROGEN, Wt% | 14.6 | 13.9 | 14.2 |
| FREEZE POINT, °F | -81.4 | -46.3 | -48.1 |
| D86 DISTILLATION | | | |
| Wt% | °F | °F | °F |
| IBP | 218 | 346 | 240 |
| 10 | 287 | 384 | 300 |
| 20 | 314 | 400 | 330 |
| 50 | 379 | 445 | 403 |
| 90 | 454 | 524 | 492 |
| EP | 490 | 560 | 522 |
| D2887 DISTILLATION | | | |
| Wt% | °F | °F | °F |
| IBP | 151 | 254 | 112 |
| 10 | 244 | 340 | 238 |
| 20 | 290 | 375 | 287 |
| 50 | 391 | 447 | 387 |
| 90 | 482 | 556 | 504 |
| EP | 619 | 661 | 631 |

DISCUSSION

Sample M-112 demonstrated a 60 percent aromatic saturation level with an actual reduction in freeze point. This run was particularly successful in that no measurable gas production was observed, resulting in a total weight gain of product equivalent to the quantity of hydrogen consumed. Results for Sample M-112 are shown in Tables IX-2 and IX-3.

Sample M-121 attained a 49 percent aromatic saturation level at conditions equivalent to that used for M-112. This sample, targeted for JP-8, is significantly heavier than M-112, which probably accounts for the lower saturation level attained. No change in freeze point was noted in the unit, and again, no measurable quantities of gas were produced. Results for Sample M-121 are shown in Tables IX-3 and IX-4.

Sample GC-1 was run for several material balance periods due to the larger quantities of feedstock available. Aromatic saturation was very good at 72 percent, with a 1°F increase in product freeze point. Measurable quantities of gas were, however, produced during this run. Some deactivation of the catalyst was apparent, as shown by the decreases in gravity and hydrogen consumption. A pressure increase may be required for this module to correct this deactivation situation. Results for Sample GC-1 were shown in Tables IX-3 and IX-5.

TABLE IX-2

MATERIAL BALANCE RESULTS FOR AROMATIC
SATURATION OF SAMPLE M-112

| Period | 1 | 2 |
|-----------------------------|-------|--------|
| OPERATING CONDITIONS | | |
| Temperature, °F | 504 | 500 |
| Pressure, PSIG | 200 | 200 |
| LHSV, Hr ⁻¹ | 2.00 | 2.03 |
| H ₂ Rate, SCFB | 8214 | 8210 |
| MATERIAL BALANCE | | |
| Weight Percent of Feed | | |
| H ₂ Consumed | 1.70 | 1.70 |
| C ₁ | - | - |
| C ₂ | - | - |
| C ₃ | - | - |
| C ₄ | - | - |
| C ₅ | - | - |
| Stabilized Liquid | 98.25 | 101.52 |
| Closure | 97.01 | 99.86 |
| | | |
| Hydrogen Consumption, SCFB | 911 | 904 |
| PRODUCT PROPERTIES | | |
| °API | 52.1 | 51.5 |

TABLE IX-3

PERTINENT JET FUEL SPECIFICATIONS
FOR AROMATIC SATURATE SAMPLES

| | <u>M-112</u> | <u>M-121</u> | <u>GC-1</u> |
|------------------------|--------------|--------------|-------------|
| AROMATICS, WTZ | 18.3 | 20.4 | 11.9 |
| GRAVITY, °API | 46.7 | 46.6 | 44.2 |
| HYDROGEN, WTZ | 14.6 | 13.9 | 14.2 |
| FREEZE POINT, °F | -81.4 | -46.3 | -48.1 |
| D-86 DIST, °F @ IBP | 218 | 346 | 240 |
| 10 VOL % | 287 | 384 | 300 |
| 20 | 314 | 400 | 330 |
| 50 | 379 | 445 | 403 |
| 90 | 454 | 523 | 492 |
| EP | 490 | 560 | 522 |
| D-2887 DIST., °F @ IBP | 151 | 254 | 112 |
| 10 WTZ | 244 | 340 | 238 |
| 20 | 290 | 375 | 287 |
| 50 | 391 | 447 | 387 |
| 90 | 482 | 556 | 504 |
| EP | 619 | 661 | 631 |

TABLE IX-4

**MATERIAL BALANCE RESULTS FOR AROMATIC
SATURATION OF SAMPLE M-121**

| Period | 1 | 2 | 3 |
|-----------------------------|--------|--------|--------|
| OPERATING CONDITIONS | | | |
| Temperature, °F | 504 | 506 | 506 |
| Pressure, PSIG | 200 | 200 | 200 |
| LHSV, Hr ⁻¹ | 2.07 | 2.04 | 1.80 |
| H ₂ Rate, SCFB | 9901 | 10,226 | 11,750 |
| MATERIAL BALANCE | | | |
| Weight Percent of Feed | | | |
| H ₂ Consumed | 0.19 | 0.39 | 2.28 |
| C ₁ | - | - | - |
| C ₂ | - | - | - |
| C ₃ | - | - | - |
| C ₄ | - | - | - |
| C ₅ | - | - | - |
| Stabilized Liquid | 101.80 | 101.94 | 101.92 |
| Closure | 101.40 | 101.34 | 98.83 |
| | | | |
| Hydrogen Consumption, SCFB | 246 | 246 | 246 |
| PRODUCT PROPERTIES | | | |
| °API | 46.1 | 43.7 | 43.6 |

TABLE IX-5

**MATERIAL BALANCE RESULTS FOR AROMATIC
SATURATION OF SAMPLE GC-1**

| Period | 1 | 2 | 3 | 4 | 5 |
|----------------------------|--------|--------|--------|--------|--------|
| OPERATING CONDITIONS | | | | | |
| Temperature, °F | 518 | 520 | 515 | 515 | 515 |
| Pressure, PSIG | 200 | 200 | 200 | 200 | 200 |
| LHSV, Hr ⁻¹ | 2.04 | 2.02 | 2.04 | 2.00 | 2.00 |
| H ₂ Rate, SCFB | 9800 | 9900 | 9730 | 10,040 | 10,000 |
| MATERIAL BALANCE | | | | | |
| Weight Percent of Feed | | | | | |
| H ₂ Consumed | 1.46 | 1.18 | 1.21 | 0.99 | 1.04 |
| C ₁ | - | - | - | - | - |
| C ₂ | - | - | - | - | - |
| C ₃ | 0.29 | 0.30 | 0.19 | 0.05 | 0.05 |
| C ₄ | 0.85 | 0.95 | 0.42 | 0.26 | 0.26 |
| C ₅ | 1.81 | 1.27 | 0.80 | 0.60 | 0.60 |
| Stabilized Liquid | 98.57 | 103.73 | 100.89 | 101.50 | 101.67 |
| Closure | 100.06 | 104.40 | 101.10 | 101.50 | 101.67 |
| | | | | | |
| Hydrogen Consumption, SCFB | 966 | 781 | 801 | 655 | 688 |
| PRODUCT PROPERTIES | | | | | |
| °API | 50.9 | 54.5 | 56.4 | 46.5 | 46. |

CONCLUSIONS

- The aromatic saturation module and conditions provided were adequate to produce specification levels of turbine fuel aromatics.
- Limited quantities of gas are produced.
- There is very little impact on freeze point in this module.
- Slightly higher pressures may be required to counteract a slight deactivation trend encountered for Sample GC-1.

